Tuning the Structural and Magnetic Properties of Thermally Robust Coordination Polymers

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Thermally robust materials of the M(5-X-pyrimidin-2-olate)₂ type [M = Co, X = Cl (1Cl), X = Br (1Br), X = I (1I); M = Zn, X = Cl (2Cl), X = Br (2Br), X = I (2I)] have been synthesized. Their X-ray powder diffraction structural characterization has revealed that they crystallize as 42d diamondoid frameworks, isomorphous to those of the pristine [M(pyrimidin-2-olate)]₄ analogues (1H, M = Co; 2H, M = Zn). The magnetic measurements of the 1X series at magnetic fields of 100, 300, and 5000 Oe reveal a weak ferromagnetic ordering taking place below the Néel temperature (TN ∼ 20 K), arising from spin canting phenomena of the antiferromagnetically coupled cobalt centers. Moreover, magnetic hysteresis studies carried out on the 1X series at 2 K reveal a strong dependence of both the coercive field Hc (2500, 1000, 775, and 500 Oe for 1Br, 1Cl, 1I, and 1H, respectively) and the remnant magnetization Mrem (0.0501 μB for 1Br and 1Cl, 0.0457 μB for 1I, and 0.0358 μB for 1H) on the 5-substituent of the pyrimidin-2-olates. The molecular alloys [Co(5-Y-pyrimidin-2-olate)]₂ (Y = Cl/Br, 1YBr) and [Co(5-Y’-pyrimidin-2-olate)]₂ (Y’ = Br/I, 1BI) have also been prepared and characterized, proving that they have intermediate properties. These materials combine interesting functional properties, such as chemical inertness, magnetism, photoluminescence, and (although weak) SHG activity.

Introduction

Functional coordination polymers have attracted considerable attention in the past few years because of their wide number of interesting properties.¹ The presence, in these frameworks, of transition metal ions is responsible for the incorporation of magnetic, optical, catalytic, and structural properties.² Of special interest is the construction of materials possessing simultaneously two or more of the above quoted features.³

Diazaaromatic ligands in their deprotonated forms, such as pyrazolates, imidazolates, and pyrimidinolates, have been recently coupled to metal ions in the attempt of preparing homoleptic functional materials lacking counterions in the
Thermally Robust Coordination Polymers


In this paper, we report the preparation, the X-ray powder diffraction (XRPD) structural characterization (Table 1), and the thermal, optical, and magnetic properties of the analogous three-dimensional species, assembled by employing the 5-substituted halopyrimidinolates (Chart 1), aiming to finely tune the behavior of this kind of materials by introducing a series of electron-withdrawing atoms in the para-position to the exocyclic oxygen atom of the ligand; a similar approach was indeed employed by Le Bideau et al. in vanadyl-based layered species. Indeed, the weak ferromagnetic ordering taking place at low temperature shows an interesting dependence on the halide nature.

**Experimental Section**

**Materials and Physical Measurements.** 2-Hydroxypyrimidine·HCl, N-bromosuccinimide, and N-iodosuccinimide were purchased from Aldrich. [Co(2-pymo)]n (1a), [Zn(2-pymo)]n (2a), 5-chloro-2-hydroxypyrimidine, and Zn-2-hydroxypyrimidine were prepared according to literature methods.

Microanalyses of C, H, and N were performed with a Fisons Instruments EA-1008 analyzer. Thermogravimetric and differential scanning calorimetric analyses were performed, under a reactive atmosphere of air, on Shimadzu-TGA-50H/DSC equipment, at heating rates of 20 and 10 °C min⁻¹, respectively (Scientific Instrumentation Centre of the University of Granada). Electronic spectra on polycrystalline samples were carried out on a Varian Cary UV–vis–NIR spectrophotometer in the reflectance mode (Scientific Instrumentation Centre of the University of Granada). IR spectra were recorded on a Midac FT-IR using KBr pellets. Magnetic susceptibility measurements were performed on polycrystalline samples in the 2–250 K with a quantum design MPMS XL. A liquid cooled by a flowing He gas was employed.

**Second-Order NLO Kurtz–Perry Measurements.** The 1064 nm initial wavelength of a Nd:YAG pulsed laser beam was shifted to 1907 nm by stimulated scattering in a high-pressure hydrogen cell. A portion of this beam was directed on sample-containing capillaries. The scattered radiation was collected by an elliptical mirror, filtered to select only the second-order contribution, and recollected with a Hamamatsu R928 photomultiplier tube, exciting at 350 nm. The SHG efficiency was evaluated by taking as reference the SHG signal of urea.

**Preparation of [Co(5-X-2-pymo)]n.** [Co(5-Cl-2-pymo)]n (1a), [Co(5-Br-2-pymo)]n (1b), and [Co(5-I-2-pymo)]n (1c) have been prepared by following a similar synthetic route: 2 mmol of CoCl₂·6H₂O was dissolved in distilled water (10 mL), and the corresponding 5-halo-2-hydroxypyrimidine (4 mmol dissolved in 50 mL of water) was added under stirring. The clear solutions were kept at room temperature for about 20 min, and then the pH was raised to 5.0 by addition of 1 M NaOH. The purple [Co(5-X-2-pymo)]n precipitates (1a, 1b, 1c) were filtered off and washed.
with water, ethanol, and ether. In the synthesis of the molecular 1:1 mixture of the corresponding 5-halo-2-pymo derivatives; after CoCl$_2$, H, 0.89; N, 12.34. Found: C, 20.77; H, 0.93; N, 11.89. IR ($\nu$ 1725, 1145 m, 803 m, 699 m). UV (P), 9390 (s, 4 A$^2$ 1145 m, 803 m, 731 m, 698 m). UV-vis (cm$^{-1}$): 30 490 (s), 18 250 (s, $A_4^2 \rightarrow T_1^R$ (P), 9390 (s, $A_4^2 \rightarrow T_1^R$).

**$^a$ $R_p = \sum (|F_o| - |F_c|)^2 / \sum |F_o|^2$; $R_{Bragg} = \sum (|F_o| - |F_c|)^2 / \sum |F_o|^2$; $R_{ref} = \sum (|F_o| - |F_c|)^2 / \sum |F_o|^2$, where $F_o$ and $F_c$ are the observed and calculated intensities. The summations run over i data points or n independent reflections. Statistical weights $w_i$ are normally taken as $1/\sigma_i^2$.**

**Table 1. Crystal Data and Refinement Details for Compounds [Co(5-Cl-2-pymo)$_2$]$_{12}$ (1c), [Co(5-Br-2-pymo)$_2$]$_{12}$ (1c$_{Br}$).**

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The geometries of the 5-X-2-pymo anions have been optimized at the reported $[M(2-pymo)_2]$ structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication Nos. CCDC 293137—293144. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, (+44)1223 336—033; e-mail, deposit@ccdc.cam.ac.uk).

**Thermodiffractometric Experiments.** The thermal behavior of the [M(5-X-2-pymo)_2] species was further studied by employing a custom-made heater (supplied by Officine Elettrotouchi di Tenno, Bleggio Inferiore (TN), Italy), mounted on a Bruker AXS Advance D8 diffractometer. A sequence of consecutive scans in the 17—37° in 2θ range was performed in the 20—440 °C temperature range, with steps of 20 °C. The thermal expansion coefficients have been calculated by taking into account the data acquired up to 340 °C, and the lattice parameters have been derived by whole pattern profile fitting.

**Results and Discussion**

**Synthesis, Spectroscopy, and Thermal Behavior of [Co(5-X-2-pymo)_2], (1x) and [Zn(5-X-2-pymo)_2], (2x).** The reaction of the 5-X-2-pymo ligands (5-X-2-pymo = 5-X-pyrimidin-2-olate) with the proper metal salt in an aqueous medium results in the precipitation of microcrystalline powders of M(5-X-2-pymo); formula $[M = Co, X = Cl (1x); X = Br (1Br), X = I (1i); M = Zn, X = Cl (2c); X = Br (2br), X = I (2i)].$ Analogously, anhydrous species of formula $M(2-pymo)_2 (M = Co, 1h, and M = Zn, 2h$) were directly precipitated using the parent 2-pymo ligand.16

The most remarkable feature of the IR spectra for the 1x and 2x species is that the ν(CO) stretching bands appear at lower wavenumbers compared to free 5-X-2-pymo ligands (Table 2). The weakening of the C=O bond can be attributed to intermolecular contacts involving the exocyclic oxygen atom (of the O—X type, as later shown by X-ray diffraction).27

The 1x species are deep purple colored, which is characteristic of tetrahedral Co(N$_4$) chromophores, when the N atoms belong to strongly coordinating heterocyclic anions.28 Indeed, their electronic spectra show two intense absorption bands (see Experimental Section) corresponding to the $\pi^* \rightarrow \pi$ transition at 280—300 nm and $\pi^* \rightarrow \pi$ (ν$_1$) electronic transitions. At variance, the $\pi^* \rightarrow \pi$ one, occurring in the NIR region, (27) Preliminary results on the crystal structures of the 5-X-2-pymo ligands (X = Br and I), obtained by XRPD methods, showed X·····O contacts slightly above 2.9 Å. The same occurs for the long known chloro derivative (Furberg, S.; Solbakk, J. Acta Chem. Scand. A 1974, 28, 435). For all these species, the solid-state IR frequencies of the CO stretching fall above 1648 cm$^{-1}$.

(26) Final $R_p$, $R_{wp}$, $R_{meas}$, and $\chi^2$ agreement factors and details on data collections and analyses for 1x and 2x can be found in Tables 1 and 2.

(24) The geometries of the 5-X-2-pymo anions have been optimized at the B3LYP/6-31G(d,p) level of theory (for the iodine atom the basis set 3-21G(∗∗∗) was adopted) using the following: Gaussian 03W, revision C.02: Gaussian, Inc.: Pittsburgh, PA, 2004.


(22) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication Nos. CCDC 293137—293144. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, (+44)1223 336—033; e-mail, deposit@ccdc.cam.ac.uk).


(21) The geometries of the 5-X-2-pymo anions have been optimized at the B3LYP/6-31G(d,p) level of theory (for the iodine atom the basis set 3-21G(∗∗∗) was adopted) using the following: Gaussian 03W, revision C.02: Gaussian, Inc.: Pittsburgh, PA, 2004.


is not detectable. In the case of d⁷ tetrahedral complexes, the position of the maximum of the first electronic transition, ν₁, coincides with the value of Δc. Yet, being ν₁ undetectable in the spectra of 1 X, their values have been calculated from those of ν₂ and ν₃, by applying Dou’s method (Table 2).²⁹

The electron-withdrawing nature of the pyrimidine-2-olate substituents is responsible for a slight increase in the Δc values compared to that for 1 H. The respective values of Racah parameters B for 1 H, 1 Cl, 1 Br, and 1 I are 755, 762, 717, and 714 cm⁻¹. It should be noted the decrease in the B values according to 1 Cl > 1 Br > 1 I indicates an increase in the covalent character of the coordinative bond along the series.

We also measured the room-temperature solid-state photoluminescence spectra of the 2 Cl, 2 Br, and 2 I species, which resulted in intense emission maxima centered at about 390 nm. An additional, broad band is observed for 2 I at about 515 nm (Figure 1). To the best of our knowledge, only two types of electronic transitions have been invoked at about 515 nm (Figure 1). An additional, broad band is observed for 2 Cl, which resulted in intense emission maxima centered at about 390 nm. An additional, broad band is observed for 2 I at about 515 nm (Figure 1). To the best of our knowledge, only two types of electronic transitions have been invoked at about 515 nm (Figure 1).

The thermal stability of the title compounds has been investigated by means of DSC and TG measurements. In the case of both the 1 X and 2 X series no distinct events can be detected but decomposition. For the species 1 Cl, 1 Br, and 1 I, decomposition is responsible for sharp weight losses on the TG diagrams, starting at 420, 450, and 350 °C, respectively. Similar sharp weight losses characterize the TG diagrams of the species 2 Cl, 2 Br, and 2 I, with Tₜₙₙₙₙ at 410, 430, and 330 °C. At least in the case of 1 Cl, 2 Cl, 1 Br, and 2 Br, these observations once again strengthen our early findings on the high thermal robustness of metal pyrimidin-2-olates, a feature to be taken into consideration when practical applications are searched for. Indeed, decomposition temperatures as high as 560 and 570 °C are reached in the case of 1 H and 2 H.¹⁶ The decrease in Tₜₙₙₙₙ on passing from 1 to 2 H to 1 to 2 X may be due to the presence of the halides, which facilitate the pyrimidine ring activation during the decomposition process: the dissociation energies of the pyridine–X bond (taken as a model of the present pyrimidine–X one) have indeed values of 464, 405, 337, and 272 kJ mol⁻¹ for X = H, Cl, Br, and I, respectively.³¹ Despite of the different dissociation energies of the C–Cl and C–Br bonds, our observation leads to an unexpected comparable stability of the chlorine and bromine derivatives (vide infra for a possible structural interpretation).

Crystal Structures and Thermidiffractometric Studies of [Co(5-X-2-pymo)₂]₂ (1X) and [Zn(5-X-2-pymo)₂]₂ (2X) Materials. (a) Crystal Structures. The asymmetric units of the isomorphous [M(5-X-2-pymo)₂]₂ compounds are composed by (a portion of) one metal center, lying about a 4 symmetry site (a Wyckoff position) and half an organic ligand, lying about a 2-fold axis parallel to a or b (d Wyckoff position) and passing through the exocyclic oxygen and halide atoms. Each metal center, showing a tetrahedral stereochemistry, is coordinated by four nitrogen atoms of the slightly longer tetrahedral ionic radius of Zn(II) vs Co(II) (0.60 vs 0.58 Å).³²

The N,N'-exo-bidentate coordination mode is, by far, the most common one adopted by the parent 2-pymo ligand¹⁵,¹⁶,³³ yet not by its 5-nitro derivative. The latter, in the few cases

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in which has been employed, has not infrequently shown its exocyclic oxygen atom coordinated to the metal center.

The bridging mode adopted by the organic moiety results, in both 1X and 2X, in a non-interpenetrated diamondoid network (see Figure 3, where just the metal centers, taken as vertexes, and the N,N’-bridges, as edges, appear). The same three-dimensional architecture has already been found in the parent [M(2-pymo)2]n species (M = Co, Zn). Notably, in the case of [Ni(2-pymo)2]n, which is not isomorphous with the analogues of Co(II) and Zn(II), a diamondoid network can be nevertheless recognized when just the overall connectivity is taken into consideration. At variance, the homoleptic [M(NP)2]n derivatives (M = Co, Zn; NP = 5-nitro-2-pyrimidinolate; see Chart 1) deviate from this trend: indeed, they crystallize as two-dimensional slabs in which the metal center shows a MN3 O stereochemistry.

Within the 1X and 2X series the X substituent plays a nonnegligible role on the unit cell volume and on the anisotropic distortion of the crystal lattice. As expected, within a single 1X or 2X series, the unit cells inflate on increasing the size of the halide (see Table 2). Yet, due to the special position about which the organic ligands lie (i.e., the C–X vectors being strictly parallel to the crystallographic axes a or b), the influence of X on the length of the crystallographic axes a and c is distinct, with c surprisingly shrinking with increasing size of the halide (see Figure 4).

This effect can be easily understood with reference to the actual location and symmetry of the bridging 5-X-2-pymo ligands, as described hereafter:

(a) The larger covalent and van der Waals radii of I vs Br and Cl and the orientation of the C–X vectors parallel to a (and b) induce larger a (and b) unit cell dimensions for the largest halide (Figure 4 and Table 2).

(b) 5-X-2-pymo-bridged pairs of metals lie in (XM, YM, ZM) and (1/2 + XM, YM, 1/4 + ZM), with a dMM intermetallic distance of

\[ d_{\text{MM}} = \left[ (a\Delta x)^2 + (b\Delta y)^2 + (c\Delta z)^2 \right]^{1/2} = \left[ (a/2)^2 + (c/4)^2 \right]^{1/2} \]

(c) Assuming a substantial constancy of the M–N distances and of the N–M–N angles (witnessed by the values reported in Table 2), d_{\text{MM}} should be insensitive to the halide nature.

(d) Therefore, the lengthening of a must be compensated by the shortening of the c axis. This is indeed the effect shown in Figure 4 and in Table 2, where the increase of the cell volume is differently attributed to the coherent changes in a and b (increasing with halide size) and in c (shrinking with it). Notably, even the parent [M(2-pymo)2]n analogues (M = Co, Zn) adhere to this scheme.

This system thus appears to be rather flexible, in that it can adapt itself to the large perturbation induced by the 5-X substituents as if it were a pantograph. As a further proof of this behavior, we also successfully precipitated Co(II) species containing an equimolar ratio of either the 5-Cl- and 5-Br-2-pymo ligands or the 5-Br- and 5-I-2-pymo ones. As expected, a (poly)crystalline solid solution was observed in both cases (1ClBr and 1BrI, respectively), with the lattice parameters nicely fitting the observed trends (see Figure 4), with no ligand segregation. These molecular alloys may open the route to the preparation of finely tuned mixed systems, where the properties of the end members can be suitably varied by using the appropriate components in the proper stoichiometry.

The structural features discussed above can be interpreted by observing that, in all species 1X and 2X, significantly short O⋯X halogen “bonds”, well below 3.0 Å (Table 2), are present along a and b. In a compilation of halogen bonds characteristics, Metrangolo and Resnati have clearly shown that their strength is higher for the heaviest halides (Cl < Br < I). Thus, the apparent erratic O⋯X values (Br < Cl < I, Figure 5a) may result from a combination of different and competing factors such as (1) the increase of the atomic size, (2) the increase of the halogen bond strength, and (3) the geometrical restraints imposed by the 3D-framework but

Figure 3. Representation of the three-dimensional diamondoid motif in [M(5-X-2-pymo)2]n. Metal centers are represented as spheres, and 5-X-2-pymo ligands, as sticks.

Figure 4. Evolution of a (top) and c lattice parameters (normalized to those of the 1H and 2H species) on varying X in the [M(5-X-2-pymo)]n series (X = H, Cl, Cl/Br, Br, Br/I, and I; M = Co, Zn). The data have been plotted vs the sum of the van der Waals and covalent radii of X (Å). The green triangle, blue square and magenta circle, red diamond refer to Co and Zn, respectively.

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not from (4) experimental uncertainties. The rather indisputable short O•••Br distance in 1 Br and 2 Br, coupled to the independent observations of short M•••M contacts (Figure 5b), seems to indicate, in both cases, an optimized situation. This is indeed counterparted by the decomposition temperatures of the 1 Br and 2 Br species, mentioned above, which are the highest within this class of compounds.

(b) Thermodiffractometric Experiments. In search for information about the dynamics of the ligands within the lattice, we also determined the thermal expansion coefficients on one of the [M(5-X-2-pymo)2]n species (namely 2 Cl; see the Experimental Section for details on the measurements). As supported by the DSC and TG traces, no formation of intermediate phases is observed before decomposition. As emerging from the Le Bail refinements of the acquired diffractograms, on passing from room temperature to 340 °C, the unit cell inflates, because of anisotropic thermal expansion, by about 1.5%, almost exclusively due to an increase of the c axis (1.0%, vs 0.3% of a). The measured thermal expansion coefficients (δln(V)/δT = 48 × 10⁻⁶, δln(a)/δT = 8 × 10⁻⁶, and δln(c)/δT = 30 × 10⁻⁶ K⁻¹) clearly suggest that, on an increase of the temperature, the 5-X-2-pymo ligands swing preferentially about the M•••M hinge, vibrating up and down the z direction.

Magnetic Properties of the Cobalt(II) Pyrimidinolate Polymers. The magnetic susceptibility of the microcrystalline samples 1 H–1 I has been measured at different fields (100, 300, and 5000 Oe) in the temperature range 2–250 K (Figure 6). The thermal dependence of the magnetic susceptibility (χM) in the high-temperature region is very similar in all cases, showing a steady increase upon cooling and no dependence with the applied external field. This behavior is consistent with an antiferromagnetic behavior for cobalt(II) systems with a ⁴A₂ ground state. However, in the low-temperature region and below the Néel temperature (TN = 20–23 K) a clear dependence of the susceptibility with the applied external field is observed, showing a sharp increase in the χM values for the 100 Oe (Figure 6a) and 300 Oe measurements. Likewise, the χM/T values steadily decrease upon cooling until the Néel temperature TN = 20–23 K is reached. At lower temperatures, the χM/T values sharply increase, with the curves reaching maxima around 15–19 K (Figure 6b).

(37) Because the X•••O distance depends essentially on the well-defined a lattice parameter; indeed, the crystal packing can be alternatively described by a family of collinear chains of halopymo ligands running along a (and b), orthogonally interconnected by the metal nodes.
The high temperature ($T > 50$ K) behavior of the magnetic susceptibility for $\text{In}_h - \text{I}_l$ can be fitted to the Curie–Weiss expression

$$\chi_M = \frac{C}{(T - \Theta)} \quad [C = N g^2 \mu^2 S(S + 1)/3k]$$

obtaining $C = 2.48(1)$ emu K mol$^{-1}$ and $\Theta = -45.3(4)$ K for $\text{In}_h$, $C = 2.53(1)$ emu K mol$^{-1}$ and $\Theta = -42.0(5)$ K for $\text{In}_c$, $C = 2.51(1)$ emu K mol$^{-1}$ and $\Theta = -45.0(5)$ K for $\text{In}_r$, and $C = 2.58(1)$ emu K mol$^{-1}$ and $\Theta = -43.2(6)$ K for $\text{In}_f$, which agrees with antiferromagnetic exchange taking place through the $N,N'$-pyrimidinolate bridges. It should be noted that the nature of the halide substituent does not have any significant effect on the magnetic exchange in the high-temperature range. The $\mu_{\text{eff}}$ values, calculated from the $C$ values obtained from the Curie–Weiss fitting of the magnetic susceptibility (Table 2), are similar (within 2%) to those obtained by taking into account their $A_2$ state, according to the expression

$$\mu_{\text{eff}} = (1 - 4\alpha/\Delta)(4S(S + 1))^{1/2} = (1 - 4\alpha/\Delta)\mu_{\text{SO}}$$

i.e. 4.357, 4.354, 4.350, and 4.353 $\mu_B$ for $\text{In}_h$, $\text{In}_c$, $\text{In}_r$, and $\text{In}_f$, respectively.\(^{38}\)

At variance, as previously mentioned, the low-temperature measurements carried out at the $\text{In}_h - \text{I}_l$ materials at different field strengths clearly show that below the Néel temperature, $T_N$, their magnetic behaviors are highly dependent on the applied field.

The experimental observation of residual magnetic moments at temperatures approaching 0 K can be interpreted by a weak ferromagnetic effect due to spin-canting,$^{53,40}$ which is allowed despite the high-symmetry crystallographic structure and the special location of the magnetic centers: indeed, a thorough symmetry analysis shows that any tilting angle between the spins in the tetragonal plane is possible.$^{40}$ For a molecular system isostructural (but not isomorphous) to the $\text{In}_h - \text{I}_l$ ones the same canting effect has been observed.$^{40}$ Magnetic hysteresis studies carried out at 2 K are also consistent with a weak ferromagnetic ordering taking place below the Néel temperature $T_N$ (Figure 6c). However, it should be noted that, despite the related nature of the $\text{In}_h - \text{I}_l$ materials, the area of each hysteresis cycle is markedly different, depending on the functionalization of the pyrimidinolate derivative. Thus, the coercive fields $H_{\text{c,coe}}$ decrease in the following sequence 2500, 1000, 775, and 500 Oe for $\text{In}_r$, $\text{In}_c$, $\text{In}_f$, and $\text{In}_h$, respectively, while the remnant magnetization $M_{\text{rem}}$ follows the trend 0.0501 $\mu_B$ for $\text{In}_r$ and $\text{In}_c$, 0.0457 $\mu_B$ for $\text{In}_f$, and 0.0358 $\mu_B$ for $\text{In}_h$. The spin-canted nature of the magnetic behavior of $\text{In}_h - \text{I}_l$, rather than a regular ferromagnetic behavior, is supported by the fact that the highest magnetizations obtained at 2 K and at an applied field of 50 kOe are significantly lower than the theoretical saturation value of 3 $\mu_B$,\(^{41}\) namely 0.356, 0.353, 0.412, and 0.408 $\mu_B$ for $\text{In}_h$, $\text{In}_c$, $\text{In}_r$, and $\text{In}_f$, respectively. Taking into account the remnant magnetization values, from the expression $\sin \theta = (M_{\text{rem}}/M_{\text{sat}}) \times 3$, canting angles in the range 2°–3° can be estimated for compounds $\text{In}_h - \text{I}_l$.\(^{42}\) The sharp rise in the susceptibility values below 20–23 K is accompanied by both real and imaginary components of the ac-susceptibility measured in a 1 Oe field oscillating at 1200 Hz centered at 22, 22.5, 20.5, and 19 K for $\text{In}_h$, $\text{In}_c$, $\text{In}_r$, and $\text{In}_f$, respectively (Figure 6d), which are due to the spin-canting phenomena. In addition, the $\text{In}_h$ and $\text{In}_f$ ac curves have anomalous real and imaginary components at about 6 K, which may be attributed to an additional long range ordering taking place.\(^{43}\)

The peculiar magnetic behavior of the $\text{In}_h - \text{I}_l$ materials can be related to the synergistic effects exerted by the acetic crystal structure, the magnetic anisotropy of the cobalt(II) centers, and the anisotropic structural distortions introduced by the 5-substituents of the pyrimidine-2-olate bridges. The lack of a monotonic behavior of the magnetic properties (vs the atomic number or the electronegativity of the X-substituent) described above cannot be rationalized; however, as commented below, it must be related to the overall anomalous performances of the bromine derivatives.

**Nonlinear Optical Properties.** Testing the second harmonic generation (SHG) efficiencies on unsieved powders of the $1_X$ and $2_X$ series ($X = \text{Cl}, \text{Br}$, and $\text{I}$) via the Kurtz–Perry powder method,$^{44}$ working with an incident wavelength of 1907 nm, resulted in almost undetectable signals with respect to standard urea. As a consequence, a quantitative evaluation of the efficiency of the single species is not available. Thus, the only achievable information is a rough division into two categories when the signal of urea is saturated, the $2_X$ compounds always showing a higher response than the $1_X$ ones.\(^{45,46}\) The weakness of the SHG signals for such highly polarizable ligands can be interpreted on a structural basis since, for symmetry reasons, the $X – \text{Ar} – \text{O}$ \textit{dipole} cannot concur to the bulk hyperpolarizability tensor.

Indeed, using the approximation proposed by Zyss et al.$^{47}$ according to the 42m crystallographic class of the $1_X$ and $2_X$ species ($X = \text{Cl}, \text{Br}$, and $\text{I}$), respectively, the anomaly real and imaginary components at about 6 K, which may be attributed to an additional long range ordering taking place.\(^{43}\)


(45) In the case of $\text{In}_h$ and $2_X$, slightly better performances and the opposite trend were observed (16), yet using a different incident wavelength (1064 nm), at which the efficiency of the purple-colored Co(II) species might be overestimated, due to contributions from fluorescence emissions. New measurements were thus performed at 1907 nm: a “new” $2_X > 1_X$ trend was now detected, nicely reproducing the general $1_X > 1_X$ one here determined.

(46) For the sake of completeness, it must be said that the $2_X$ species ($X = \text{Cl}, \text{Br}$, and $\text{I}$) photodecompose.

species, the only nonvanishing component of the bulk second-order nonlinearity/molecule ($b_{\text{eff}}$) has the expression $b_{\text{eff}} = \beta_{\text{CT}} \sin \psi \cos \psi \sin^2 \theta \cos \theta$, $\psi$ and $\theta$ being the polar coordinates of $\beta_{\text{CT}}$, the molecular hyperpolarizability. If the $X-\text{Ar}-O$ “dipole” is taken as the major charge-transfer axis (CT) of the system, $\theta$ (90°) and $\psi$ (either 0 or 90°) imply $b_{\text{eff}} = 0$. Consequently, our scarce, but nonzero, signal arises from other electronic transitions which are not symmetry-forbidden, possibly involving the metal centers.

Conclusions

In this report we have shown the fine-tuning of the structural and physicochemical properties (thermal stability and magnetic hardness) of a series of isomorphous, diamondoid frameworks of the [M(5-X-2-pymo)$_2$]$_n$ type by varying the halide substituent in the 5 position of the pyrimidine ring. The steric demand of these substituents is responsible for a slight perturbation of the crystal cell parameters but not for a change in either the coordination of the metal center or the overall framework topology.

In all isomorphous frameworks, the pyrimidinolates transmit the antiferromagnetic coupling between the Co(II) ions; however, the uncompensated antiferromagnetic couplings arising from the diamondoid topology [as in Co(4-azaben-zimidazolate)$_2$]$^{39a}$] leads to spin-canting phenomena that are sensitive to the structural characteristics. Indeed, a significant enhancement of the magnetic hardness takes place in the halo-substituted derivatives compared to the pristine $1_1$ species.

Another remarkable feature of these materials is their high thermal stability: although lower than the pristine [M(2-pymo)$_2$]$_n$, it is still considerably high even in the case of the most activated ones, $1_1$ and $2_1$.

Interestingly, halogen bond strength, thermal decomposition temperatures, and magnetic measurements coherently indicate that the bromo derivatives enhance these functional properties, thus showing that halide substitution does not imply monotonic changes of these physicochemical features.

The values of the halogen bond interactions also explain why the [M(5-nitro-2-pymo)$_2$]$_n$$^{34a}$ materials necessarily adopt a different structure: no space would be left in the rather dense diamondoid packing for the bulkier nitro group. It would be therefore interesting to prepare 5-amino- or 5-hydroxy-substituted pyrimidinols (with smaller X substituents), to verify the possibility of building extended frameworks, isomorphous to $1_X-2_X$, containing linear chains of H-bonded motifs.

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Supporting Information Available: Final Rietveld refinement plots for species $1_X$ and $2_X$ ($X = \text{Cl}, \text{Br}, \text{and I}$). This material is available free of charge via the Internet at http://pubs.acs.org.