Heterometallic Mn$^{III}_{4}$Ln$_2$ (Ln = Dy, Gd, Tb) Cross-Shaped Clusters and Their Homometallic Mn$^{III}_{4}$Mn$^{II}_{2}$ AnalOGues

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ABSTRACT: The employment of di-2-pyridyl ketone, (py)$_2$CO, in heterometallic Mn/4f and homometallic Mn cluster chemistry has yielded six Mn$^{III}_{4}$Ln$_2$ and two Mn$^{III}_{4}$Mn$_2$ structurally related clusters, namely, [Mn$_4$Ln$_2$((py)$_2$CO)$_2$]$_4$(NO$_3$)$_2$$(R$CO$_2$)$_2$(H$_2$O)$_6$(NO$_2$)$_2$(Ln = Gd, Tb; R = Et, Me, 5), [Mn$_4$Dy$_2$((py)$_2$CO)$_2$]$_4$(EtCO$_2$)$_2$(H$_2$O)$_6$(MeOH)]•0.7MeOH•0.8H$_2$O (6), [Mn$_4$Co$_2$((py)$_2$CO)$_2$]$_4$(EtCO$_2$)$_2$(H$_2$O)$_6$(MeOH)]•0.7MeOH•0.8H$_2$O (7), [Mn$_4$Mn$_2$((py)$_2$CO)$_2$]$_4$(EtCO$_2$)$_2$(H$_2$O)$_6$(MeOH)]•0.7MeOH•0.8H$_2$O (8), and [Mn$_6$O$_2$((py)$_2$CO)$_2$]$_4$(NO$_3$)$_2$$(py)$_4$•2MeOH (9), where (py)$_2$CO$_2$$^{2-}$ is the dianion of the gem-diol derivative of (py)$_2$CO. The compounds possess a new type of cross-shaped structural core, which in the case of 1–6 is essentially planar, whereas in 7 and 8 it deviates from planarity. Clusters 1–6 are rare examples of Mn/4f species bearing (py)$_2$CO or its derivatives, despite the fact that this ligand has been well-studied and proven a rich source of more than 200 metal compounds so far. Variable-temperature, solid-state direct-current and alternating-current magnetization studies were performed on complexes 1–5, 7, and 8 revealing that the dominant exchange interactions between the metal ions are antiferromagnetic and indicating ground-state spin values of $S = 5$ (for 1), $6$ (for 5), and $2$ (for 7 and 8).

INTRODUCTION

The synthesis and characterization of 3d/4f polynuclear compounds have gained significant attention in recent times owing to their relevance to different research areas, including molecule-based magnetic materials and magnetic refrigerants. In the former field, such species often behave as single-molecule magnets (SMMs) exhibiting super-paramagnet behavior below a blocking temperature $T_B$. Their properties originate from intrinsic structural and electronic characteristics of their metal cores, such as the large ground-spin state ($S$) and the large and negative Ising (or easy-axis) type of magnetooisotropy $D$. SMMs are good candidates for many technological applications including high-density information storage, molecular spintronics, and qubits for quantum computation. Further, quantum mechanical phenomena have been identified in SMMs, such as spin-state entanglement, spin-phonon coupling, spin-parity effects, both thermally assisted and pure quantum tunneling of the magnetization (QTM), quantum phase interference, and others.

Most 4f ions exhibit large single-ion anisotropy and several unpaired electrons, providing all the requirements for a compound to behave as an SMM. Indeed, many 3d/4f SMMs have been reported, including Fe/4f, Co/4f, Ni/4f, Cu/4f, and Cu/4f $^{3}$ compounds. However, the majority of 3d/4f SMMs are Mn/4f clusters bearing some Mn$^{III}$ centers with their $S = 2$ spin state and a significant uniaxial anisotropy. Many Mn/Ln SMMs are now known, for example, Mn$_{11}$Ln$_4$, Mn$_{12}$Gd$_{16}$, Mn$_{11}$Gd$_{17}$, Mn$_{11}$Ln$_4$, Mn$_{11}$Dy$_{18}$, and Mn$_{11}$Dy$_{18}$ species. Some of these compounds display enhanced SMM properties, such as the Mn$_{12}$Tb$_2$ cluster with $U_{eff} = 103$ K, and the Mn$_{12}$Dy$_2$ cluster with $U_{eff} = 74$ K comparable to that of the Mn$_{12}$ family of SMMs, the first discovered and most studied species to date.

3d/4f metal clusters are also of special importance in the field of magnetic refrigerants. Magnetic refrigeration is a cooling technique, which is based on the magnetocaloric effect (MCE). It is defined as the response of a ferri- or ferromagnet to an external magnetic field causing the change of its temperature. There are now known several species displaying enhanced MCE, the majority of which contain the $^{1}$Gd$^{III}$ ion, since it provides zero magnetic anisotropy, as well as weak exchange interactions favoring the presence of low-lying spin states. High-nuclearity 3d/4f clusters, such as Co$_{16}$Gd$_{24}$, Co$_{16}$Gd$_{24}$, Cu$_{16}$Gd$_{24}$, Mn$_{12}$Gd$_{12}$ (M = Co$^{III}$/Ni$^{III}$), Ni$_{20}$Gd$_{20}$, and Ni$_{20}$Gd$_{20}$ have been reported to display enhanced cooling properties. Among them, Co$_{10}$Gd$_{14}$ and Ni$_{10}$Gd$_{12}$ exhibit impressively large.

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MCEs, revealing their potential for use as magnetic coolers in the ultralow temperature range.

From the above-mentioned, clearly 3d/4f metal clusters are very promising for the development of new species with enhanced magnetic properties. However, for this to be realized, it is very crucial to gain extensive knowledge on the way that 4f ions affect the properties of the isolated compounds. In this context, scientists working in this field are mainly focused on the isolation of low nuclearity compounds that are amenable to an in-depth magnetic analysis. Indeed, a lot of work has been done and has provided valuable information on how the isotropic or anisotropic nature of the 4f ion involved affects the nature and magnitude of the exchange interactions, as well as the dynamics of slow relaxation of magnetization in low-nuclearity compounds. However, the number of heterometallic compounds that are amenable to this approach is highly restricted by the nuclearity of the studied species. An alternative approach in this direction, which could be applied to polynuclear 3d/4f metal clusters, is based on the generation of a “library” that includes isostructural 3d/4f heterometallic and 3d homometallic clusters, that is, clusters with the same metal core and same bridging ligands that possibly differ in the terminal ligation. Comparison of the properties of homometallic and heterometallic compounds with identical or very similar structural features would definitely provide new insights for the magnetic understanding of metal clusters and SMMs. However, this approach is still in its infancy, and in fact there have been very few heterometallic compounds that possess the same structural core as homometallic clusters; these are mostly confined to tetrnnuclear compounds with a “butterfly” topology. Herein, we report the synthesis and characterization of six MnLn4 (Ln = Dy, Tb, Gd) and their homometallic Mn6 structural analogues. The reported compounds possess an uncommon cross-shaped metal core and bear a di-2-pyridyl ketone (py)_2CO derivative as the primary chelating organic ligand. Notably, although (py)₂CO has been extensively studied in 3d and 3d/4f metal cluster chemistry, the reported compounds are uncommon Mn/Ln species containing this ligand. Furthermore, direct current (dc) and alternating current (ac) magnetic susceptibility studies were performed on representative compounds and revealed that one of the Mn₄Dy₂ compounds displays out-of-phase ac tails revealing the existence of a slow relaxation of the magnetization process at very low temperatures.

### EXPERIMENTAL SECTION

**Synthesis.** All manipulations were performed under aerobic conditions using materials as received. Mn(ETCO₂)₂·2H₂O, [MnO·(ETCO₂)₂((py)₂CO)]ClO₄, and NBu₄MnO₄ were prepared as previously reported. Caution! Although no such behavior was observed during the present work, perchlorate, nitrate, azide, and organic permannenate salts are potentially explosive; they should be synthesized and used in small quantities and treated with care.

[Mn₄Dy₂{(py)₂CO₄}₂(NO₃)₄(ETCO₂)₂(H₂O)₆](NO₃)₂ (2). This was prepared in the same manner as complex 1 but using Dy(NO₃)₃·6H₂O (0.399 g, 0.88 mmol) instead of Gd(NO₃)₃·6H₂O. After two weeks, X-ray quality orange crystals of 2-solvents were collected by filtration, washed with MeCN (2 × 5 mL) and Et₂O (2 × 5 mL), and dried under vacuum. Yield: ~60%. Anal. Calcd (Found) for 2: C, 31.95 (32.52); H, 2.90 (3.18); N, 8.94 (9.26%). Selected IR data (KBr, cm⁻¹): 3737 (m), 3145 (w), 2926 (w), 1585 (m), 1529 (m), 1483 (m), 1388 (s), 1313 (m), 1277 (m), 1209 (m), 1061 (s), 1032 (w), 978 (w), 939 (w), 901(w), 874 (w), 806 (w), 785 (w), 766 (m), 667 (m), 609 (s), 538 (m), 438 (w), 419 (w).

[Mn₄Dy₂{(py)₂CO₄}₂(NO₃)₄(ETCO₂)₂(H₂O)₆](NO₃)₂ (3). This was prepared in the same manner as complex 1 but using Tb(NO₃)₃·6H₂O (0.400 g, 0.92 mmol) instead of Gd(NO₃)₃·6H₂O. After three weeks, X-ray quality crystals of 3-solvents were collected by filtration, washed with MeCN (2 × 5 mL) and Et₂O (2 × 5 mL), and dried under vacuum. Yield: ~60%. Anal. Calcd (Found) for 3: C, 32.07 (32.52); H, 2.91 (3.18); N, 8.98 (9.29%). Selected IR data (KBr, cm⁻¹): 3732 (m), 3144 (w), 2926 (w), 1585 (m), 1525 (m), 1485 (m), 1391 (s), 1314 (m), 1227 (m), 1207 (m), 1061 (s), 1032 (w), 978 (w), 938 (w), 902 (w), 876 (w), 803 (w), 785 (w), 768 (w), 669 (m), 603 (s), 538 (m), 439 (w), 418 (w).

[Mn₄Dy₂{(py)₂CO₄}₂(NO₃)₄(ETCO₂)₂(H₂O)₆](MeOH): 0.7MeOH·0.8H₂O (4·0.7MeOH·0.8H₂O). Solid Dy(NO₃)₃·6H₂O (0.100 g, 0.22 mmol) was added to a stirred solution of Dy(NO₃)₃·6H₂O (0.201 g, 0.21 mmol) and (py)₂CO (0.100 g, 0.419 g, 0.81 mmol) in MeOH (10 mL). The resulting red solution was stirred for 40 min, filtered, and the filtrate was left in an open flask. Slow evaporation of the filtrate at room temperature yielded orange crystals of 4.0·MeOH·0.8H₂O, which were kept in mother liquor for X-ray analysis, or collected by filtration and dried under vacuum for other solid-state studies. Yield: ~60%. Anal. Calcd (Found) for 4: C, 32.78 (33.04); H, 3.00 (3.27); N, 8.87 (9.09%). Selected IR data (KBr, cm⁻¹): 3395 (m, b), 2759 (w), 1576 (m), 1477 (m), 1450 (m), 1386 (s), 1302 (m), 1219 (w), 1155 (w), 1072 (s), 1016 (m), 897 (w), 817 (w), 771 (m), 697 (m), 670 (m), 651 (m).

[Mn₄Dy₂{(py)₂CO₄}₂(NO₃)₄(Me₂CO)₂(H₂O)₆](0.8H₂O). To a stirred solution of N-butylmethylenamine (bdeaH₂) (0.160 mL, 0.98 mmol) and (py)₂CO (0.099 g, 0.54 mmol) in MeCN (20 mL) was added solid Mn(Me₂CO)₃·4H₂O (0.250 g, 1.02 mmol), which caused a rapid color change to red. The mixture was left under stirring for 15 min, Gd(NO₃)₃·6H₂O (0.402 g, 0.89 mmol) was added, and the resulting solution was stirred for a further 3 h. Solid NBu₄MnO₄ (0.101 g, 0.28 mmol) was then added in small portions, the solution was left under stirring for 15 min, filtered, and the filtrate was left in an open flask. Slow evaporation of the solvent at room temperature gave orange crystals of 5-solvents, which were kept in mother liquor for X-ray analysis or collected by filtration and dried under vacuum. Yield: ~60%. Anal. Calcd (Found) for 5: C, 31.31 (31.64); H, 2.74 (3.09); N, 9.13 (9.25%). Selected IR data (KBr, cm⁻¹): 3408 (m, b), 2850 (w), 1590 (m), 1520 (m), 1473 (m), 1430 (m), 1384 (s), 1301 (m), 1219 (w), 1155 (w), 1103 (w), 1070 (m), 1045 (s), 895 (w), 812 (m), 777 (m), 694 (m), 670 (m), 636 (m), 565 (w).

[Mn₄Gd₂{(py)₂CO₄}₂(NO₃)₄(C₂H₅ClO₂)₂(MeOH):(py)₂]-·2MeOH (5·2MeOH). To a stirred solution of C₂H₅ClO₂Na (0.180 g, 1.01 mmol) and (py)₂CO (0.099 g, 0.54 mmol) in MeOH/py (20/5 mL) was added Mn(NO₃)₃·4H₂O (0.251 g, 1.00 mmol), which caused a rapid color change to dark red. The solution was left under stirring for 15 min, and then Gd(NO₃)₃·6H₂O (0.402 g, 0.89 mmol) was added. The red solution was stirred for a further 2 h and filtered, and the filtrate was left in an open flask. Slow evaporation of the solvent at room temperature gave orange crystals of 6·2MeOH, which...
were kept in mother liquor for X-ray analysis, or collected by filtration and dried under vacuum. Yield: ∼45%. Anal. Calcd (Found) for 6: C, 39.13 (39.61); H, 2.72 (2.89); N, 9.13 (8.93%). Selected IR data (KBr, cm⁻¹): 3390 (s, b), 2950 (w), 1776 (s, b), 1612 (m), 1506 (m), 1362 (m), 1250 (m), 1123 (s), 971 (w), 920 (w), 813 (w), 755 (s), 703 (w), 670 (m), 631 (w), 606 (w), 555 (w), 538 (w), 518 (w), 499 (w), 449 (w), 429 (w), 419 (s, m), 409 (w). Method A. To a solution of H₂pd (0.300 mL, 4.15 mmol) in MeCN/py (20/2 mL) was added Mn(NO₃)₂ (0.751 g, 2.99 mmol) resulting in a dark red solution. The solution was stirred for a further 20 h and filtered, and the filtrate was left in an open flask. Slow evaporation led to the formation of red crystals of 7-4H₂O, which were left in contact with the mother liquor for X-ray analysis, or collected by filtration and dried under vacuum. Yield: ∼60%. Anal. Calcd (Found) for 7: C, 39.45 (39.17); H, 3.10 (3.26); N, 12.98 (13.17%). Selected IR data (KBr, cm⁻¹): 3390 (s, b), 2950 (w), 2883 (w), 1603 (m), 1543 (w), 1485 (w), 1443 (m), 1303 (w), 1221 (w), 1148 (s), 1086 (s), 1014 (s), 812 (w), 787 (w), 752 (m), 704 (m), 670 (m), 573 (w), 540 (w), 507 (w), 409 (w).

Method B. Method A was repeated without the addition of pdH₂. Slow evaporation of the solvent at room temperature gave red crystals (yield: ∼60%). The product was identified as 7-4H₂O by IR spectral comparison with authentic material and from unit cell determinations.

Table 1. Crystallographic Data for Complexes 1–8

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were kept in mother liquor for X-ray analysis, or collected by filtration and dried under vacuum. Yield: ∼45%. Anal. Calcd (Found) for 6: C, 39.13 (39.61); H, 2.72 (2.89); N, 9.13 (8.93%). Selected IR data (KBr, cm⁻¹): 3385 (m, b), 2860 (w), 1582 (m), 1530 (m), 1498 (w), 1435 (m), 1392 (s), 1323 (w), 1215 (w), 1127 (w), 1104 (m), 1078 (m), 1053 (s), 971 (w), 920 (w), 813 (w), 755 (s), 703 (w), 670 (m), 631 (w), 606 (w), 555 (w), 538 (w), 518 (w), 499 (w), 449 (w), 429 (w), 419 (s, m), 409 (w). Method A. To a solution of H₂pd (0.300 mL, 4.15 mmol) in MeCN/py (20/2 mL) was added Mn(NO₃)₂·6H₂O (0.750 g, 2.95 mmol) under stirring resulting in the formation of a dark red solution. This solution was stirred for 5 min, and then (py)₆CO (0.099 g, 0.54 mmol) and HCO₂Na (0.067 g, 0.98 mmol) were added under vigorous stirring. The solution was stirred for a further 20 h and filtered, and the filtrate was left in an open flask. Slow evaporation led to the formation of red crystals of 7-4H₂O, which were left in contact with the mother liquor for X-ray analysis, or collected by filtration and dried under vacuum. Yield: ∼60%. Anal. Calcd (Found) for 7: C, 39.45 (39.17); H, 3.10 (3.26); N, 12.98 (13.17%). Selected IR data (KBr, cm⁻¹): 3390 (s, b), 2950 (w), 2883 (w), 1603 (m), 1543 (w), 1485 (w), 1443 (m), 1303 (w), 1221 (w), 1148 (s), 1086 (s), 1014 (s), 812 (w), 787 (w), 752 (m), 704 (m), 670 (m), 573 (w), 540 (w), 507 (w), 409 (w).
(x,b) 3100 (w) 2950 (w), 1601 (s), 1474 (m), 1435 (s), 1383 (s), 1298 (m), 1238 (w), 1219 (w), 1113 (w), 1099 (w), 1076 (s), 1020 (s,b), 3100 (w) 2950 (w), 1601 (s), 1474 (m), 1435 (s), 1383 (s),

**Method A.** Method A was repeated without the addition of pPh3. Slow evaporation of the solvent led to the formation of red crystals (yield ~ 60%). The product was identified as 8 by IR spectral comparison with authentic material and from unit cell determinations.

**X-ray Crystallography.** Data were collected on an Oxford- Diffraction SuperNova diffractometer equipped with a CCD area detector and a graphite monochromator utilizing Mo Kα radiation (λ = 0.71073 Å). Selected crystals were attached to glass fiber with paratone-N oil and transferred to a goniostat for data collection. Empirical absorption corrections (multiscan based on symmetry-related measurements) were applied using Crysalis RED software.28

The structures were solved by direct methods using SIR9229 and refined on F2 using full-matrix least-squares using SHELXL9729 and SHELXL-2014/7.29. Software packages used: CrysalisCCD28 for data collection, CrysalisRED28 for cell refinement and data reduction, WINGX for geometric calculations,29d while DIAMOND30a and MERCURY30b were used for molecular graphics. The program SQUEEZE,31 a part of the PLATON package of crystallographic software, was used to remove contribution of highly disordered solvent molecules in 1–5 and 8. Although many experiments were performed to grow better quality crystals of compounds 2–4 and several crystallographic data sets were also collected, the NO3− counterions were highly disordered in every case, thus their contribution was removed using the program SQUEEZE.31 For all compounds, the non-H atoms were treated anisotropically, whereas the H atoms were placed in calculated, ideal positions and refined as riding on their respective C atoms. In some cases, the H atoms of the H2O and MeOH solvent molecules could not be located. Unit cell parameters and structure solution and refinement data for complexes 1–8 are listed in Table 1.

**Physical Studies.** Infrared spectra were recorded in the solid state (KBr pellets) on a Shimadzu Prestige-21 spectrometer in the 4000–400 cm−1 range. Variable-temperature dc and ac magnetic susceptibility data were collected at the University of Florida using a Quantum Design MPMS-XL SQUID susceptometer equipped with a 7 T magnet and operating in the 1.8–300 K range. Samples were embedded in solid eicosane to prevent torquing. The ac magnetic susceptibility measurements were performed in an oscillating ac field of 3.5 G and a zero dc field. The oscillation frequencies were in the 5–1488 Hz range. Pascal’s constants were used to estimate the diamagnetic corrections, which were subtracted from the experimental susceptibilities to give the molar paramagnetic susceptibility (χm). The absence of a systematic study of the Mn/4f(14f) system is noticeable considering the great development of this research field over the recent years. On the basis of this, we decided to use of (py)2CO in Mn/4f carbonyl chemistry exploring its potential to yield new high-nuclearity clusters and SMMs.

The reaction of Mn(ETCO2)2·2H2O, Ln(NO3)3·6H2O (Ln = Gd, 1; Dy, 2; Tb, 3), (py)2CO, and NEt3 in the presence of 1,3-propanediol (Hpd) afforded a red dark solution from which well-shaped orange crystals of compounds 1–3 with the general formula 

$$\text{[Mn}_4\text{Ln}_2\text{O}_6\text{(py)}_2\text{CO}_2\text{NO}_3\text{(EtCO}_2)_2\text{(H}_2\text{O})_6\text{]}\text{(NO}_3\text{)}_2$$

were subsequently isolated. The formation of 1–3 is summarized in eq 1. (py)2CO exists in its diamionic gem-diolate form, (py)2CO2−, whose formation involves a nuclophilic attack by the H2O molecule on the carbonyl group.

$$\text{4Mn(ETCO}_2)_2\text{2H}_2\text{O} + 2\text{La(NO}_3\text{)}_3\text{6H}_2\text{O} + 4\text{(py)}_2\text{CO} + \text{O}_2$$

$$\rightarrow$$

$$\text{[Mn}_4\text{La}_2\text{O}_6\text{(py)}_2\text{CO}_2\text{NO}_3\text{(EtCO}_2)_2\text{(H}_2\text{O})_6\text{]}\text{(NO}_3\text{)}_2 + 8\text{H}^+ + 6\text{ETCO}_2^- + 2\text{NO}_3^- + 10\text{H}_2\text{O}$$

$$\text{(Ln = Gd, 1; Dy, 2; Tb, 3)}$$

(1)

After the crystallographic characterization of 1–3, which revealed that they possess aesthetically pleasing structures with a rare metal topology, this reaction system was investigated in detail. Thus, many reactions were performed involving the employment of different metal sources, as well as various RCOOH (R = Me, Et, C6H5Cl) leading to the isolation of three new compounds, namely, $$\text{[Mn}_3\text{Dy}_2\text{O}_6\text{(py)}_3\text{ClO}_4\text{]}$$, $$\text{[Mn}_4\text{Gd}_2\text{O}_6\text{(py)}_2\text{CO}_2\text{NO}_3\text{(EtCO}_2)_2\text{(H}_2\text{O})_6\text{]}\text{(NO}_3\text{)}_2$$, and $$\text{[Mn}_4\text{Gd}_2\text{O}_6\text{(py)}_2\text{CO}_2\text{NO}_3\text{(C}_6\text{H}_5\text{CICO}_2)_2\text{(MeOH)}_2\text{(py)}_2\text{]}$$ that are structurally related to 1–3. The formation of 4–6 is summarized in eqs 2–4. In particular, the reaction of 

$$\text{[Mn}_4\text{O}_6\text{(EtCO}_2)_2\text{(py)}_2\text{]}\text{(ClO}_4\text{]}\text{, Dy(NO}_3\text{)}_3\text{6H}_2\text{O and (py)}_2\text{CO in MeOH yielded a dark red solution, from which orange crystals of 4 were isolated after a few days. The reaction of Mn(MeCO}_2)_2\text{4H}_2\text{O, Gd(NO}_3\text{)}_3\text{6H}_2\text{O, (py)}_2\text{CO, N-butylidethanolamine (bdcaH}_2\text{)}$$

and NBu4MnO4 in MeCN provided access to compound 5, whereas the reaction of Mn(NO3)3·4H2O, Gd(NO3)3·6H2O, (py)2CO, and C6H5CICOOHNa in MeOH/py (4:1 v/v) afforded a dark red solution, from which compound 6 was isolated in fairly high yield. We note that the formation of 5 can also take place without the addition of NBu4MnO4 which facilitates the oxidation of Mn; however, longer stirring time is required, whereas the yield of the reaction is much lower. The aliphatic diols that were added in the reaction mixtures that yielded clusters 1–3 and 5 played a crucial role in their synthesis and/or isolation; experiments in the absence of diols have led to amorphous materials that could not be further characterized.

$$\text{4[Mn}_4\text{O}_6\text{(EtCO}_2)_2\text{(py)}_2\text{]}\text{(py)}_2\text{]}\text{(ClO}_4\text{]} + 6\text{Dy(NO}_3\text{)}_3\text{6H}_2\text{O} + 12\text{(py)}_2\text{CO} + 12\text{MeOH}$$

$$\rightarrow$$

$$3[\text{Mn}_4\text{Dy}_2\text{O}_6\text{(py)}_2\text{CO}_2\text{ClO}_4\text{]}\text{(EtCO}_2)_2\text{(MeOH)}_2\text{]} + 12\text{pyH}^+ + 16\text{H}^+ + 6\text{NO}_3^- + 4\text{ClO}_4^- + 18\text{ETCO}_2^- + 22\text{H}_2\text{O}$$

(2)

$$\text{4Mn(MeCO}_2)_2\text{4H}_2\text{O} + 2\text{Gd(NO}_3\text{)}_3\text{6H}_2\text{O} + 4\text{(py)}_2\text{CO} + \text{O}_2$$

$$\rightarrow$$

$$3[\text{Mn}_4\text{Gd}_2\text{O}_6\text{(py)}_2\text{CO}_2\text{NO}_3\text{(EtCO}_2)_2\text{(H}_2\text{O})_6\text{]}\text{(NO}_3\text{)}_2 + 8\text{H}^+ + 6\text{ETCO}_2^- + 2\text{NO}_3^- + 18\text{H}_2\text{O}$$

(3)

$$\text{4Mn(NO}_3\text{)}_3\text{4H}_2\text{O} + 2\text{Gd(NO}_3\text{)}_3\text{6H}_2\text{O} + 4\text{(py)}_2\text{CO}$$

$$\rightarrow$$

$$2\text{C}_6\text{H}_5\text{CICO}_2\text{NaO} + 4\text{O}_2 + 2\text{MeOH} + 2\text{pyH}$$

(4)

$$\rightarrow$$

$$3[\text{Mn}_4\text{Gd}_2\text{O}_6\text{(py)}_2\text{CO}_2\text{NO}_3\text{(C}_6\text{H}_5\text{CICO}_2)_2\text{(MeOH)}_2\text{(py)}_2\text{]}\text{(py)}_2\text{]} + 24\text{H}_2\text{O} + 8\text{H}^+ + 2\text{Na}_2 + 10\text{NO}_3^-$$

(4)

The unusual cross-shaped metal core that is observed in clusters 1–6 is thermodynamically favored, as evidenced by the fact that these compounds were obtained under a variety of reaction conditions. As a consequence, the isolation of the structurally related homometallic mixed-valent Mn4 com-
Pounds, namely, \([\text{Mn}_6\text{O}_2((\text{py})_2\text{CO}_2)_4(\text{H}_2\text{O})_4](\text{ClO}_4)_4\) (7) and \([\text{Mn}_8\text{O}_2((\text{py})_2\text{CO}_2)_4(\text{NO}_3)_4(\text{py})_4]\) (8), was also feasible. In particular, the reaction of Mn(ClO\text{4})_2\cdot x\text{H}_2\text{O}, (\text{py})_2\text{CO}, \text{HCO}_2\text{Na}, \text{NaN}_3, \text{and H}_2\text{pd} in \text{MeCN/py} yielded a dark red solution from which 7 was isolated, whereas the reaction of Mn(NO\text{3})_2\cdot 4\text{H}_2\text{O}, (\text{py})_2\text{CO}, \text{MeCO}_2\text{Na}, \text{NaN}_3, \text{and H}_2\text{pd} in \text{EtOH/py} provided access to 8. The stoichiometric reactions that afforded compounds 7 and 8 are summarized in eqs 5 and 6.

\[
\begin{align*}
6\text{Mn(ClO}_4\text{)}_2 + 4(\text{py})_2\text{CO} + \text{O}_2 + 8\text{H}_2\text{O} + 4\text{py} & \rightarrow [\text{Mn}_8\text{O}_2((\text{py})_2\text{CO}_2)_4(\text{H}_2\text{O})_4](\text{ClO}_4)_4 \quad (7) \\
+ 8\text{H}^+ + 8\text{ClO}_4^-& 
\end{align*}
\]

\[
\begin{align*}
6\text{Mn(NO}_3\text{)}_2 + 4\text{H}_2\text{O} + 4(\text{py})_2\text{CO} + \text{O}_2 + 4\text{py} & \rightarrow [\text{Mn}_8\text{O}_2((\text{py})_2\text{CO}_2)_4(\text{NO}_3)_4(\text{py})_4] \quad (8) \\
+ 8\text{H}^+ + 8\text{NO}_3^- + 20\text{H}_2\text{O} & 
\end{align*}
\]

Note that after the determination of the crystal structures of compounds 7 and 8, which revealed that H_2pd is absent from the final products, their synthesis was successfully repeated without the addition of H_2pd in the reaction mixture.

**Description of Structures.** Representations of the molecular structure and the structural core of 1 are shown in Figure 1. Selected interatomic distances and angles are listed in Table 2. Compounds 1–6 possess related structures containing the same \([\text{Mn}^{III}\text{Ln}_2(\mu_2^\prime\text{O})_2(\mu_\text{OR})_4]^{10+}\) core (Ln = Gd, 1, 5; 6–2MeOH; Dy, 2, 4; Tb, 3). Thus, only the structure of 1 will be described in detail, and it will be compared to those of 2–6.

**Table 2. Selected Interatomic Distances (Å) and Angles (deg) for 1**

- Mn(1)–O(1): 1.853(3) Gd(1)–O(6): 2.388(4)
- Mn(1)–O(1)°: 1.856(3) Gd(1)–O(7): 2.502(4)
- Mn(1)–O(2): 1.936(3) Gd(1)–O(2°): 2.367(3)
- Mn(1)–O(5): 2.157(4) Gd(1)–O(10): 2.393(4)
- Mn(1)–O(16): 1.946(3) Gd(1)–O(11): 2.428(5)
- Mn(2)–O(1°): 2.003(3) Gd(1)–N(1): 2.568(5)
- Mn(2)–O(3): 1.865(4) Gd(1)–N(4°): 2.593(4)
- Mn(2)–O(4): 1.861(4) Mn(1)–Mn(1°): 2.803(5)
- Mn(2)–O(12): 2.187(4) Mn(1)–Gd(1): 3.416(5)
- Mn(2)–N(3): 2.089(4) Gd(1)–Gd(1°): 4.907(5)
- Mn(2)–N(2): 2.098(4) Mn(2)–Mn(2°): 6.434(5)
- Mn(1)–O(16)–Gd(1°): 104.7(2) Mn(1)–O(1)–Mn(1°): 98.2(2)
- Mn(1)–O(2°)–Gd(1): 104.6(2) Mn(1°)–O(1)–Mn(2°): 131.1(2)
- Mn(1)–O(1)–Mn(2°): 130.8(2)

*Symmetry transformations used to generate equivalent atoms: (i) −x + 2/3, −y + 1/3, −z + 1/3.

**Figure 1.** Structure of the cation of 1 (top) and its \([\text{Mn}^{III}\text{Ln}_2(\mu_2\text{O})_2(\mu_\text{OR})_4]^{10+}\) structural core (bottom). Color code: Mn^{III}, blue; Gd^{III}, pink; O, red; N, green; C, gray. The hydrogen atoms and solvent molecules were omitted for clarity.

**Scheme 1.** Crystallographically Established Coordination Mode of (py)_2CO_2^{2−} in Complexes 1–8

One at each side. All the metal and O atoms in the structural core of 1 are arranged in an almost planar configuration with the largest deviation from the mean plane defined by the metal and O atoms of the core being ~0.18 Å for Mn1 (and Mn1’; Figure 2, left).

The two Gd^{III} ions are nine-coordinate with their coordination spheres being completed by two η_1^′\eta_1^′\mu_1\text{EtCO}_2^{−} ions, two chelating NO_3^{−} ions, and four H_2O molecules. Mn2 and Mn2’ are six-coordinate displaying a distorted octahedral geometry, and their coordination sphere is completed by two additional H_2O molecules. Mn1 (and Mn1’) is five-coordinate with square pyramidal geometry; the OS (and OS’) atom of the propionate ion occupies the apical position. The Mn oxidation states and the protonation level of O_2^{2−} were confirmed by charge considerations, bond-valence sum (BVS) calculations (BVS calculations for Mn and O atoms gave values 2.81 and 3.16 for Mn^{III} and 1.81 for O^{2−}), and the observation of Jahn–Teller distortions at the octahedral Mn^{III} ions.
The crystal structure of 1 is stabilized by strong hydrogen bonds between the O atoms of terminally ligated H2O molecules (O12), which act as donors, and O atoms of NO3 counterions (O14), which act as acceptors [O12...O14 = 2.86(2) Å]. The cations of 1 are relatively well-isolated with the shortest metal--metal number of vertices; thus, the main semiregular three-dimensional figures that may be considered are the octagonal pyramid, the heptagonal bipyramid, and five Johnson polyhedra (capped cube, capped square antiprism, tricapped trigonal prism, tridiminished icosahedron, triangular cupola). The best fit was obtained for a tricapped trigonal prism.

The crystal structure of 1 was deduced by the program SHAPE. The coordination of two additional NO3•••− in 4.07MeOH·0.8H2O and 6·2MeOH are neutral instead of cationic (1). The charge balance is achieved by the coordination of two additional NO3− in 4.07MeOH·0.8H2O and 6·2MeOH, which in case of 1 act as counterions; (iii) the terminal ligations: one MeOH and three H2O molecules in 4·0.7MeOH·0.8H2O, two MeOH and two py in 6·2MeOH, instead of six H2O molecules in 1; and (iv) the kind of the carboxylate ligand: MeCO2− in 5 and ClPhCO2− in 6·2MeOH, instead of EtCO2− in 1.

Representations of the molecular structure and the structural core of compound 7·4H2O are shown in Figure 3, and selected interatomic distances and angles are listed in Table 3.

**Figure 2.** Structural cores of 1 (left) and 7 (right) emphasizing the relative planarity of the metal and O atoms. Color code: MnIII, blue; MnII, yellow; GdIII, pink; O, red. N, green; C, gray. The H atoms and solvent molecules were omitted for clarity.

**Figure 3.** Structure of the cation of 7 (left) and its [MnIII4MnIII2(μ3−O)2(μ−OR)4]8+ structural core (right). Color code: MnIII, blue; MnII, yellow; O, red; N, green; C, gray. The H atoms and solvent molecules were omitted for clarity.

**Table 3. Selected Interatomic Distances (Å) and Angles (deg) for 7·4H2O**

<table>
<thead>
<tr>
<th>Distance/Angle</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn(1)−O(4)</td>
<td>2.141(7)</td>
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<tr>
<td>Mn(1)−O(3)</td>
<td>2.152(5)</td>
</tr>
<tr>
<td>Mn(1)−O(2)</td>
<td>2.175(3)</td>
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<td>Mn(1)−N(1)</td>
<td>2.301(4)</td>
</tr>
<tr>
<td>Mn(2)−O(5)</td>
<td>1.866(3)</td>
</tr>
<tr>
<td>Mn(2)−O(4)</td>
<td>1.882(3)</td>
</tr>
<tr>
<td>Mn(2)−N(2)</td>
<td>2.203(6)</td>
</tr>
<tr>
<td>Mn(3)−O(1)</td>
<td>1.892(3)</td>
</tr>
<tr>
<td>Mn(1)−O(2)−Mn(2)</td>
<td>103.9(2)</td>
</tr>
<tr>
<td>Mn(2)−O(5)−Mn(3)</td>
<td>131.2(2)</td>
</tr>
<tr>
<td>Mn(2)−O(5)−Mn(2)</td>
<td>97.6(2)</td>
</tr>
</tbody>
</table>

Symmetry transformations used to generate equivalent atoms: (·) x, −y, −z; (′) −x + 2, −y, −z; (″) −x + 2, y, z.

Complex 7·4H2O crystallizes in the orthorhombic space group Cmca. Its structure consists of a [MnO43−(py)2CO2−·(py)4(H2O)4]+ cation, ClO4− counterions, and H2O solvent molecules. The centrosymmetric cation possesses a cross-shaped [MnIII4MnIII2(μ3−O)2(μ−OR)4]8+ core, which is similar to the one present in compounds 1−6 with the LnIII ions being replaced by MnII ions. However, in this case the core is distorted; thus, the Mn and O atoms do not adopt a planar configuration as happens with the structural cores of 1−6. In particular, the structural core of 7·4H2O consists of a planar [Mn3(μ−O−O)2]8+ butterfly unit that is linked through four η4:η′4:η′4:η′4 ligands to two MnII ions (Mn1 and Mn1′), lying 1.60 (2) Å above and below the plane defined by the atoms of the [Mn4(μ3−O)4]18+ butterfly core (Figure 2, right).

The coordination sphere of the metal ions is completed by four py and four H2O molecules. The MnII and two of the MnIII ions (Mn3 and its symmetry equivalent) are six-coordinate with distorted octahedral geometry, whereas the remaining MnIII...
atoms (Mn2 and its symmetry equivalent) are five-coordinate adopting a square pyramidal coordination geometry. The Mn oxidation states and the protonation level of O2− ions were determined by charge considerations, BVS calculations32 (BVS calculations for Mn and O atoms gave values 3.01 and 3.02 for MnIII, 1.97 for MnII and 1.93 for O2−), and the observation of Jahn–Teller distortions for the octahedral MnIII ions, which take the form of axial elongation of the N3–Mn3–N3' and the symmetry equivalent axes.

Closer inspection of the crystal structure of 7-H4H2O reveals that there are strong H-bonding interactions involving the bound and lattice H2O molecules, alkoxy groups of (py)2CO2−, and O atoms of ClO4− counterions. Although there are extended H-bonding interactions in 7-H4H2O, there are no direct H-bonds linking neighboring Mn6 units, and, as a result, these are fairly well-separated with the shortest metal···metal distance between neighboring molecules of 7-H4H2O being 8.438 Å (Mn1···Mn1).

The structure of compound 8 (Figure S6) is similar to that of 7-H4H2O, with the main difference being the replacement of the four terminal H2O molecules in 7-H4H2O by four nitro ligands in 8; as a result, 7-H4H2O is a cationic, whereas 8 is a neutral compound. Furthermore, there are no significant intermolecular interactions in 8.

Compounds 1−6 are uncommon examples of Mn/Ln clusters bearing di-2-pyridyl ketone, (py)2CO. (py)2CO is a very well-studied organic ligand with rich coordination chemistry that has led to a variety of homometallic and heterometallic clusters with interesting structural features and magnetic properties.26 However, very few Mn/Ln clusters with this ligand or any of its derivatives have been reported.26c Thus, 1−6 fill an important literature gap providing new insights for the coordination chemistry of (py)2CO. In addition, they have been observed before in mixed metal cluster chemistry.25 The same structural core, although slightly distorted, is observed in the homometallic clusters 7-H4H2O and 8; in addition, the latter bear (py)2CO2−, which adopt the same coordination mode as in the case of 1−6. Thus, the reported MnIII4MnII3 compounds and MnIII2LnII2 represent an uncommon collection of homometallic compounds (7 and 8) and their heterometallic analogues (1−6) possessing related crystal structures, which display novel structural features.

**Magnetic Susceptibility Studies.** Solid-state, variable-temperature dc magnetic susceptibility (χM) data were collected on vacuum-dried microcrystalline samples of complexes 1−5, 7, and 8 suspended in eicosane to prevent torquing, in the 5.0−300 K range in a 0.1 T (1000 Oe) magnetic field, and they are shown in Figure 4 as χM vs T plots for complexes 1−5, 7, and 8. For complexes 1−5, 7, and 8, the χM vs T plots are similar and consistent with dominant antiferromagnetic (AF) intramolecular exchange interactions. Note that antiferromagnetic interactions are very common in MnIII−Gd and other 3d−4f species possessing unoccupied 3d−j,j+1 orbital, for example, CoII (low spin)−Gd, EuII−Gd.23a,c,55

For the homometallic compounds 7 and 8, the χM vs T value at 300 K is much lower (7, 13.02 cm3 mol−1 K; 8, 15.09 cm3 mol−1 K) than the calculated spin-only (g = 2.00) value of 20.75 cm3 mol−1 K expected for two MnIII and four MnIII non-interacting ions, indicating the existence of strong antiferro-
magnetic exchange interactions between the metal centers. $\chi_M T$ steadily decreases with decreasing temperature to 50 K (7, 9.85 cm$^3$ mol$^{-1}$ K, 8, 11.57 cm$^3$ mol$^{-1}$ K) and then more rapidly to 3.85 cm$^3$ mol$^{-1}$ for 7, and to 4.75 cm$^3$ K mol$^{-1}$ for 8, at 5.0 K. The $\chi_M T$ values at low temperature are indicative of a very low or diamagnetic ground state for both compounds.

Magnetization ($M$) data were also collected for 1, 5, 7, and 8 in the 0.1–7 T and 1.8–10.0 K ranges, and these were plotted as reduced magnetization ($M/N_{\text{eff}}$) versus $H/T$ (Figures S7 and S8). We collected data at a wide range of magnetic fields, including low-field data to avoid problems caused by the existence of low-lying excited states and/or intermolecular interactions. However, it was not feasible to obtain a good quality fit assuming that only the ground state is populated in this temperature range. This reveals that the complexes possess low-lying excited states, populated even at these relatively low temperatures.

The ac susceptibility studies were performed on complexes 1–5, 7, and 8 in the 1.8–15 K region in zero applied field with a 3.5 Oe driving field to probe for slow magnetization relaxation. The ac susceptibility data for complex 4, shown as $X_M'$ versus $T$ in Figure 5, top, were collected at various frequencies. The values at high temperatures agree closely with the dc susceptibility data at the same temperature. The $X_M'$ decreases continuously with decreasing temperature up to ~3 K as was also observed in the dc plot, suggesting the depopulation of excited states as temperature is lowered. Below 3 K a slight frequency-dependent drop is observed, which is combined with the presence of a tail in the out-of-phase ac plot ($X_M''$ [Figure S5, bottom]) indicating that 4 may display a slow relaxation process at very low $T$ indicative of single-molecule magnetism behavior. The ac susceptibility studies of complexes 1–3 and 5 ($X_M T$ vs $T$, Figures S9–S12) are in good agreement with the dc data at the same temperature range. However, no frequency-dependent drop is seen in the in-phase plots at low temperatures, and consequently no signal is observed in the ac out-of-phase plots ($X_M''$ Figures S9–S12) indicating that complexes 1–3 and 5 do not display SMM behavior.

The ac susceptibility studies use no dc field being an excellent complementary tool for determining the ground-state spin value $S$ by avoiding potential complications from a large dc field. The in-phase susceptibility $X_M'$ data for 1 (Figure S9) and 5 (Figure S12) reveal that the $X_M T$ values are ~15.9 and ~22.6 cm$^3$ mol$^{-1}$ K at 15 K, remain almost constant down to ~7 K, and then decrease to ~12.8 and 17.5 cm$^3$ mol$^{-1}$ K, respectively, at 1.8 K. Extrapolation of the $X_M T$ signal to 0 K from $T > ~7$ K (to avoid the effects of intermolecular interactions at lower temperatures) gives values of ~14.1 and ~21 cm$^3$ mol$^{-1}$ K for 7 and 1.8 K, respectively, at 1.8 K. Extrapolation of the $X_M T$ signal to 0 K from $T > ~7$ K (to avoid the effects of intermolecular interactions at lower temperatures) gives values of ~14.1 and ~21 cm$^3$ mol$^{-1}$ K for 7 and 1.8 K, respectively, at 1.8 K. Extrapolation of the $X_M T$ signal to 0 K from $T > ~7$ K (to avoid the effects of intermolecular interactions at lower temperatures) gives values of ~14.1 and ~21 cm$^3$ mol$^{-1}$ K for 7 and 1.8 K, respectively, at 1.8 K.

Finally, as expected, on the basis of their small $X_M T$ value, complexes 7 and 8 do not exhibit out-of-phase ac signals down to 1.8 K (Figures S13 and S14) and thus are not SMMs.

It is noteworthy that the heterometallic Mn$^{II}_{4}$Gd$^{II}$ complexes 1 and 5 display different ground-state spin values (1, $S_T = 5$; 5, $S_T = 6$) that are significantly larger than that of the homometallic complexes 7 and 8 ($S_T = 2$). A possible explanation for the observed spin variability could come from the comparison of the crystal structures of the Mn$^{II}_{4}$Gd$^{II}$ and Mn$^{III}_{4}$Mn$^{II}_{2}$ complexes. All compounds comprise a [Mn$^{III}_{4}$($\mu_3$-O)$_{10}$]$^{6+}$ butterfly unit, which is linked either to two Gd$^{III}$ ions (in 1 and 5) or to two Mn$^{II}$ ions (in 7 and 8), one at each side. The magnetic interactions between the Gd$^{III}$ ions (for 1 and 5) and the central Mn$^{III}_{4}$ structural unit are expected to be very weak; thus, the former could be considered as magnetically isolated Gd$^{III}$ ions contributing an $S = 7$ to the total spin of the compounds. The rationalization of the $S_T$ values of 1 ($S_T = 5$) and 5 ($S_T = 6$) requires that their Mn$^{III}_{4}$($\mu_3$-O)$_{10}$]$^{6+}$ units possess $S = 2$ and 1 ground states, respectively. Indeed, this could be the case, since compounds possessing the planar Mn$^{III}_{4}$($\mu_3$-O)$_{10}$]$^{6+}$ butterfly core are known to exhibit spin variability due to the presence of spin frustration effects. Thus, small changes in the relevant magnitude of the competing $J_{bb}$ and $J_{ff}$ interactions ($J_{bb}$ and $J_{ff}$ refer to the inner “body–body” and outer “wing tip–body” interactions, respectively, of the Mn$^{II}_{4}$ butterfly) could result, for example, from the presence of different bridging carboxylate ligands as happens in 1 (Et$\text{CO}_2$) and 5 (Me$\text{CO}_2$), which can affect significantly their spin ground state, which, as a result, can vary from $S_T = 0$ to $S_T = 8$. Thus, the spin variability observed in the Mn$^{III}_{4}$Gd$^{II}$ complexes is attributed to the planar Mn$^{III}_{4}$($\mu_3$-O)$_{10}$]$^{6+}$ unit in their structure, which is well-known to display various $S_T$ values due to spin frustration effects.

In addition, the homometallic Mn$^{II}_{4}$ compounds exhibit lower ground-state spin values ($S_T = 2$) than the corresponding
Mn₉Gd₄ (Sₚ = 5, 6) ones. This can be attributed to a number of reasons including (i) the higher spin contribution from Gd³⁺ than Mn²⁺, (ii) different metric parameters (bond lengths and angles) of the compounds due to the presence of Mn³⁺ (in 7 and 8) instead of Gd³⁺ ions (in 1, 5) and (iii) stronger exchange interactions of the two terminal metal ions (Mn³⁺ in 7, 8 and Gd³⁺ in 1, 5) with the Mn³⁺₄ planar butterfly, in the case of the homometallic complexes.

### CONCLUSIONS

The synthesis, structures, and magnetic properties of six heterometallic Mn³⁺₄Ln₂ metal clusters (1–6) and their homometallic Mn³⁺₄Mn³⁺₄ (7 and 8) structural analogues are discussed. The compounds bear the anionic gem-diolate form of di-2-pyridyl ketone as organic ligand, and most of the heterometallic ones (1–3, 5) were prepared from a reaction procedure that involves use of a combination of (py)₂CO with aliphatic diols in Mn₄/4f carboxylate chemistry. Although the diols do not appear in the final product they play a crucial role in the isolation of the Mn₄Ln₂ compounds, since reactions in their absence did not result in their formation. In fact this is the initial systematic investigation on the use of a combination of (py)₂CO with diols for the isolation of new Mn-containing complexes. The reported compounds display an uncommon cross-shaped metal core, which appears for the first time in both the heterometallic 3d/4f metal cluster chemistry and in the coordination chemistry of (py)₂CO. The isolation of a series of clusters possessing this uncommon cross-shaped core is unexpected, since it reveals its stability and the easiness of its formation something that is not in line with the literature findings. Similarly, the isolation of both the homometallic Mn₄ and the heterometallic Mn₄Ln₂ analogues is rather surprising, especially if we take into account that these compounds display uncommon structural cores. The difficulty to isolate homometallic 3d and heterometallic 3d/4f complexes possessing related cores arises mainly from the larger coordination numbers of the 4f ions and also from the significant difference in the size of 3d and 4f metal ions.

The dc and ac magnetic susceptibility measurements in representative compounds revealed the presence of dominant antiferromagnetic exchange interactions. The Mn₉Gd₄ compounds display spin ground-state values Sₚ = 5 (1) and 6 (5), whereas the homometallic Mn₄ compounds (7 and 8) show Sₚ = 2. On the other hand, the spin variability in the case of the two heterometallic complexes was attributed to the presence of the planar [Mn³⁺₄(μ₁-O)₂]₈⁺ butterfly unit in their structure, which is weakly coupled to the two Gd³⁺ ions and is well-known to display various Sₚ values from 0 to 8 due to spin frustration. On the other hand, the Mn₉ compounds display a significantly smaller Sₚ for a number of reasons discussed in the magnetism section, as expected, since they are different compounds. In addition, one of the Mn₉Dy₂₃ compounds (4) displays weak out-of-phase ac signals (χ″) at low temperatures indicating that it might be a weak SMM.

Thus, (py)₂CO, after many years of intense research efforts that have yielded an impressive number of compounds bearing this ligand or its derivatives, remains a wellspring of new metal clusters with novel structural features and interesting magnetic properties. The combination of (py)₂CO with diol-type ligands is demonstrated as a powerful synthetic method toward the isolation of new 3d and 3d/4f metal clusters that will definitely afford several new compounds both homometallic and heterometallic in the near future. Further studies toward the synthesis of Mn and Mn/Ln clusters with (py)₂CO combined with diol-type ligands are in progress and will be reported in due course.

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.7b00191.

Structural figures for 2–6 and 8, and magnetism plots (PDF) Crystallographic data for complexes 1–8 (CIF) Crystallographic data (CIF) Crystallographic data (CIF) Crystallographic data (CIF) Crystallographic data (CIF) Crystallographic data (CIF) Crystallographic data (CIF)

### AUTHOR INFORMATION

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### Notes

The authors declare no competing financial interest.

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