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Structural diversity ranging from oligonuclear complexes to 1-D and 2-D coordination polymers generated by tetrasubstituted adamantane and spirobifluorene derivatives

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Dedicated to Professor Cristian Silvestru, on the occasion of his 65th birthday

Abstract:

Using tetrahedral and tetragonal spacers, seven new complexes have been obtained: $[\text{Co}(\text{hfac})_2(\text{L}^1)_{0.5}]$ **1**, $[\text{Cu}_2(\text{hfac})_4\text{L}^2]$ **2**, $[\text{Co}(\text{hfac})_2\text{L}^2]$ **3**, $[\text{Co}(\text{hfac})_2(\text{L}^2)_{0.5}] \cdot 8\text{H}_2\text{O}$ **4**, $[\text{AgL}^2](\text{SbF}_6) \cdot \text{CH}_3\text{COOC}_2\text{H}_5$ **5**, $[\text{Mn}(\text{hfac})_2(\text{L}^3)_{0.5}]$ **6**, $[\text{Zn}(\text{OAc})_2(\text{L}^3)_{0.5}]$ **7**, ($\text{L}^1 = 1,3,5,7$ -tetrakis(4-cyanophenyl)adamantane, $\text{L}^2 = 2,2',7,7'$ -tetracyano-9,9'-spirobifluorene and $\text{L}^3 = 2,2',7,7'$ -tetra(4-pyridyl)-9,9'-spirobifluorene, Hhfac = hexafluoroacetylacetone). Compound **1** exhibits a 2-D grid-like structure with the tetradentate spacer acting as a 4-connecting ligand. The 2,2',7,7'-tetrasubstituted-spirobifluorene derivatives connect the $\{\text{M}^{\text{II}}(\text{hfac})_2\}$ entities into a binuclear complex (**2**), a linear chain (**3**) and diamond chains (**4**, **6**). The *cis* or *trans* configuration of the metal nodes influences the overall topology ($\text{M}^{\text{II}} = \text{Cu}^{\text{II}}$, Co^{II} , Mn^{II}). Similarly, a 1-D double chain topological motif results by linking zinc ions and L^3 in compound **7**. Compound **5** is a 2-D coordination polymer featuring a layered framework with square cavities. Compound **5** undergoes a reversible single-crystal-to-single-crystal process, with removal of the solvent molecules (ethyl acetate). The luminescent properties of compounds **5**, **7** have been investigated and reveal blue emission with maxima at 402 and 483 nm, respectively. The dynamic magnetic properties and EPR spectrum of **1** have been investigated, revealing the occurrence of slow relaxation of the magnetization that most likely involves a Raman process.

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Introduction

Tetratopic tectons are widely employed in crystal engineering. The rigid four-connecting ligands built on a tetrahedral or a tetragonal backbone, decorated with various coordinating groups, act as structural motifs in generating molecular assemblies, ranging from oligonuclear complexes to 1-D, 2-D, 3-D coordination polymers.^[1] A rich structural diversity can be rationally designed by the judicious combination of geometrically well-defined organic linkers and metal building units with particular stereochemical preferences. Several network topologies mimicking basic inorganic structural prototypes have been constructed from tetrahedral nodes: diamondoid (dia), platinum sulfide (pts), fluorite (flu), SrAl_2 (sra), etc.^[2] Tetradentate tectons built around a tetrahedral core (adamantane,^[3] methane,^[3m-q,4] silane,^[4b,m,5] germane^[5a]) are endowed with the specific orientation of the donor groups toward the corners of a tetrahedron, resulting in 3-D networks. However, 2-D systems built on tetrahedral shaped linkers have been also described.^[3j,5c,6] We have, recently, emphasized the role played by the coordination preference of the metal centre, along with the tetrahedral organic linker's symmetry, in assembling in a 3-D framework featuring a PtS topology, or a 2-D grid-like coordination polymer.^[6d]

A particular case of tetragonal tectons is represented by the 9,9'-spirobifluorene derivatives bearing functional groups grafted at positions 2,2',7,7'. The two fluorene moieties sharing a common spiro carbon atom describe an orthogonal scaffold featuring a D_{2d} symmetry. The spiro derivatives are widely used in optoelectronics,^[7] as chiral ligands,^[8] or as electropolymerizable building blocks,^[9] and yet they are rarely employed as tectons in the construction of coordination polymers,^[10] supramolecular architectures^[11] or covalent-organic frameworks (COFs)/ porous organic polymers (POPs).^[12] The interaction of the metal nodes with the spirobifluorene derivatives bearing donor groups generates structural motifs imprinted with the orthogonal arrangement of the fluorene units within the organic tecton.

Herein, we report the synthesis and structural characterization of seven new compounds constructed from $\{\text{M}^{\text{II}}(\text{hfac})_2\}$ units, Ag^+ and Zn^{2+} nodes: $[\text{Co}(\text{hfac})_2(\text{L}^1)_{0.5}]$ **1**, $[\text{Cu}_2(\text{hfac})_4\text{L}^2]$ **2**, $[\text{Co}(\text{hfac})_2\text{L}^2]$ **3**, $[\text{Co}(\text{hfac})_2(\text{L}^2)_{0.5}] \cdot 8\text{H}_2\text{O}$ **4**, $[\text{AgL}^2](\text{SbF}_6) \cdot \text{CH}_3\text{COOC}_2\text{H}_5$ **5**, $[\text{Mn}(\text{hfac})_2(\text{L}^3)_{0.5}]$ **6**, $[\text{Zn}(\text{OAc})_2(\text{L}^3)_{0.5}]$ **7**, where L^1 is a tetrahedral spacer having four 4-cyanophenyl moieties attached to an adamantane skeleton and L^2 and L^3 are 2,2',7,7'-spiro bifluorene derivatives bearing four cyano (L^2) and four phenyl-pyridyl fragments (L^3), respectively (Scheme 1). The magnetic

properties of compound **1** and the photoluminescent properties for compounds **5**, **7** were investigated.

Scheme 1

Results and discussion

Since the nitrile groups have a low coordinating ability, we have employed as assembling nodes $\{M^{II}(\text{hfac})_2\}$ units and silver cations. The electron-withdrawing fluorine atoms enhance the Lewis acidity of the metal ion and facilitate the coordination of the nitrile groups to the metal centers. The nature of the resulting network will be different as the organic tecton interacts with the metal ion either through the *trans* or the *cis* available positions. Silver(I) and zinc(II) metal ions are chosen for designing luminescent materials. By reacting L^1 , L^2 and L^3 with various $\{M^{II}(\text{hfac})_2\}$ complexes ($M^{II} = \text{Cu}^{II}$, Co^{II} , Mn^{II}), silver(I) and zinc(II) salts, (AgSbF_6 and $\text{Zn}(\text{OAc})_2$), the new coordination compounds **1–7** were assembled.

The reaction of L^1 with $[\text{Co}(\text{hfac})_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ afforded red single crystals of **1**. We have shown that the assembling of L^1 with $\{\text{Mn}(\text{hfac})_2\}$ leads to a neutral 2-D coordination polymer,

where the tetradentate ligand connects the metal species into a grid-like network.^[6d] Since the structural investigation reveals that compound **1** is isomorphous with the previously reported compound, $[\text{Mn}(\text{hfac})_2(\text{L}^1)_{0.5}]$, we will briefly discuss the case of complex **1**.

Figure 1. (a) Fragment of crystal structure of **1** showing the interaction of the tetrahedral ligand L₂ with two {Co(hfac)₂} units of opposite chiralities (symmetry code: ^a = 1-x, 0.5-y, z) (b) Perspective view of a layer of **1** constructed from metal centres of opposite chiralities (green – delta, violet – lambda configuration) (CF₃ groups were omitted for clarity); (c) Packing diagram of **2** showing the two-fold interpenetration of 2-D nets.

The Co^{II} ions are hexacoordinated with a slightly distorted octahedral geometry: four oxygen atoms from two chelating hfac⁻ anions (Co1 – O1 = 2.082(6), Co1 – O2 = 2.045(6) Å) and two ligand nitrogen atoms occupying the *cis* positions (Co1 – N1 = 2.116(8) Å) (Figure 1 a). Despite the 4-connectivity of the tetrasubstituted adamantane spacer, the *cis*-coordination of the

nitrogen atoms to the $\{\text{Co}(\text{hfac})_2\}$ units precludes the formation of a 3-D network, as expected for a *trans* configuration. Two of L^1 arms link into chains metal building blocks of same Δ configuration, while the other two arms bridge metal centers of Λ configuration. The 2-D layered structure of **1** can be described as sets of *zig-zag* chains built from metal centers of opposite chirality running perpendicular to each other (Figure 1b). Two such layers interpenetrate (Figure 1c).

Compound **2** is a neutral binuclear complex with the L^2 acting as a bidentate ligand. The two crystallographically nonequivalent Cu^{II} ions have similar coordination environments: four oxygen atoms of the chelating hfac^- ligands forming the basal plane ($\text{Cu1} - \text{O1} = 1.946(4)$, $\text{Cu1} - \text{O2} = 1.926(4)$, $\text{Cu1} - \text{O3} = 1.940(4)$, $\text{Cu1} - \text{O4} = 1.928(4)$, $\text{Cu2} - \text{O5} = 1.938(5)$, $\text{Cu2} - \text{O6} = 1.947(5)$, $\text{Cu2} - \text{O7} = 1.925(5)$, $\text{Cu2} - \text{O8} = 1.947(5)$ Å), and one nitrile nitrogen atom in the apical position ($\text{Cu1} - \text{N4} = 2.270(6)$, $\text{Cu2} - \text{N1} = 2.266(6)$ Å). The trigonal distortion from square pyramidal (SP) geometry is evaluated by the τ_5 parameter, defined as $\tau_5 = [(\theta - \varphi)/60] \times 100$, where θ and φ are the angles between the donor atoms forming the plane in a square-pyramidal geometry.^[13] The values of the τ for Cu(1) ($\tau_{5\text{Cu1}} = 11.16\%$) and Cu(2) ($\tau_{5\text{Cu2}} = 23.16\%$) ions indicate that both geometries are close to square-pyramidal (Figure 2). The fluorene units connected by the spiro carbon atom act differently: one bridges the copper(II) ions, while the other does not interact with the metal ions. The uncoordinated nitrile groups are slightly deviated from the main plane of the fluorene unit they are attached to (N2: 6.18° and N3: 6.86°)

Figure 2. Molecular structure of the binuclear complex $[\text{Cu}_2(\text{hfac})_4L^2]$ **2**.

Aiming to construct coordination polymers based on the L^2 spacer, we have chosen $[Co(hfac)_2(H_2O)_2] \cdot H_2O$ as a starting material. The organic tecton bridges the metal nodes into a 1-D linear chain in the structure of **3** (Figure 3). The stereochemistry of the Co^{II} ions is octahedral, with four oxygen atoms arising from the $hfac^-$ anions laying in the equatorial plane ($Co1 - O1 = 2.053(4)$, $Co1 - O2 = 2.053(4)$, $Co1 - O3 = 2.034(5)$, $Co1 - O4 = 2.050(4)$ Å) and two nitrogen atoms of the L^2 molecules bound in the *trans* positions ($Co1 - N1 = 2.118(4)$, $Co1 - N2^a = 2.128(4)$ Å, $a = -1+x, -1+y, z$). As in the case of compound **2**, the nitrile groups of one fluorene units remain uncoordinated. The two fluorene units are perfectly orthogonal.

Figure 3. Prespective view of the 1-D coordination framework of **3** with atom numbering scheme (symmetry code: $a = -1+x, -1+y, z$).

By increasing the metal to ligand ratio, we obtained red single crystals of $[Co(hfac)_2(L^2)_{0.5}] \cdot 8H_2O$ **4**. The tetradentate ligand coordinates in a *cis* fashion to the metal nodes. A double chain structural motif showing square loops is generated by linking the orthogonally-shaped tecton, L^2 , and an assembling metal unit with right-angled available coordination sites. The one-dimensional channels formed by the packing of the doubles chains in the crystals are filled with water molecules (Figure 4 a). Since the number of the water molecules could not be directly determined by the crystallographic measurements, we estimated the presence of eight water molecules per formula ($ESI^\dagger$) from the data obtained by elemental and thermogravimetric analyses. The Co^{II} ions adopt a distorted octahedral coordination geometry formed by four oxygen atoms belonging to the $hfac^-$ anions ($Co1 - O1 = 2.074(7)$, $Co1 - O2 = 2.024(8)$, $Co1 - O3 = 2.062(9)$, $Co1 - O4 = 2.031(7)$ Å) and two nitrogen atoms from two organic linker molecules ($Co1 - N1 = 2.177(10)$, $Co1 - N2 = 2.089(10)$ Å). The two fluorene branches of a L^2 molecule connect metal centers of different chiralities: one bridges $\{Co(hfac)_2\}$ nodes of Δ configuration, while the other fluorene branch metal ions of Λ configuration. The crystal

structure of **4** can be regarded as two *zig-zag* chains built from metal nodes of opposite chiralities joint by sp^3 spiro carbon atoms (Figure 4b).

Figure 4. (a) Detail of crystal structure of **4** showing the diamond chains; (b) 1-D double chain of **4** constructed from metal nodes of delta and lambda configurations (green – delta, violet – lambda configuration) (CF₃ groups were omitted for clarity).

To extend the dimensionality of the systems based on spirobifluorene tecton bearing nitrile groups, we have reacted L^2 with $AgSbF_6$, the SbF_6^- anion showing low coordinating ability. A 2-D coordination polymer, $[AgL^2](SbF_6) \cdot CH_3COOC_2H_5$ **5**, is built up by linking the metal ions with a tetratopic spirobifluorene derivate. The silver ions are tetra-coordinated by four nitrogen atoms belonging to four L^2 molecules ($Ag1 - N1 = 2.287(7)$, $Ag1 - N2^a = 2.259(7)$, $Ag1 - N3^b = 2.247(7)$, $Ag1 - N4^c = 2.297(7)$ Å, $^a = -1+x, -1+y, z$, $^b = x, -1+y, z$, $^c = -1+x, y, z$). The τ_4 parameter, used to describe the geometry of a four coordinated metal centre, is defined as

$\tau_4 = [360 - (\alpha + \beta)]/141$, where α and β are the two largest angles between the metal ion and the donor atoms ($\tau_4 = 0$ for ideal square planar and $\tau_4 = 1$ for ideal tetrahedral geometry, while the values for trigonal pyramid and “see-saw” geometries lie in between).^[14] The stereochemistry of the Ag^{I} ions can be described as tetrahedral, according to the value of the τ_4 index for four-coordinate complexes [$\tau_{4\text{Ag}(1)} = 0.89$]. The combination of the two 4-connected nodes generates a 2-D framework with a grid topology. The square meshes of the net are alternately occupied by solvent molecules and anions (Figure 5a). The layers are stacked in an AB fashion (Figure 5b). Interestingly, compound **5** undergoes a single-crystal-to-single-crystal transformation when heated at 90°C for 48 h. The X-ray structural analysis of **5a** reveals the removal of ethyl acetate molecules from the lattice voids without any alteration of the core structure (Figure 5c). The process is reversible, crystals **5a** transforming into **5**, by keeping them for several days in the presence of vapors of ethyl acetate.

Figure 5. (a) View of the 2-D layer in **5** along with the alternating accommodation of the square meshes (symmetry code: $^a = -1+x, -1+y, z$; $^b = x, -1+y, z$; $^c = -1+x, y, z$); (b) Detail of the packing

diagram showing the channels filled by the anions and the solvent molecules; (c) View of the 2-D layer in **5a** with the square meshes occupied only by SbF_6^- anions (symmetry code: $^a = -1+x, -1+y, z$; $^b = x, -1+y, z$; $^c = -1+x, y, z$).

Figure 6. (a) Perspective view of the crystal structure **6** (symmetry code: $a = x, -1+y, z$); (b) Representation of the *S* and *R* conformations of L^3 molecules in **6**; (c) Packing diagram of **6** showing two double chains built from the *R*-configured ligand molecules bridging metal centers of lambda configuration, and *S*-type ones and $\{Mn(hfac)_2\}$ units of delta configuration, respectively.

The reaction of L^3 with $[Mn(hfac)_2(H_2O)_2] \cdot H_2O$ afforded yellow single crystals of $[Mn(hfac)_2(L^3)_{0.5}]$ **6**. The structure of **6** consists of chains resulted by connecting $\{Mn(hfac)_2\}$ node with L^3 . A 1-D double-stranded chain structure, similar to compound **4**, arises by the coordination of a 2,2',7,7'-spirobifluorene spacer into the *cis* positions of a hexafluoroacetylacetonate complex. The Mn^{II} ions are surrounded in an octahedral coordination stereochemistry by four *hfac*[−] oxygen atoms and two nitrogen atoms from two ligand molecules ($Mn1 - O1 = 2.193(3)$, $Mn1 - O2 = 2.155(4)$, $Mn1 - O3 = 2.144(4)$, $Mn1 - O4 = 2.195(3)$, $Mn1 - N1 = 2.234(4)$, $Mn1 - N2^a = 2.243(4)$ Å, $a = x, -1+y, z$) (Figure 6 a). The pyridyl moieties are tilted with respect to the plane of the corresponding fluorene units, resulting in a different spatial orientation of the pyridyl groups towards the neighboring aryl rings within each spirobifluorene arm (figure 6b). It is interesting to notice that the *R*-configured ligand molecules bridge only metal centers of Λ configuration, while the *S*-configured ones interact with $\{Mn(hfac)_2\}$ units of Δ configuration (Figure 6c). The double chains stack in staggered fashion.

The reaction of L^3 and zinc acetate yielded yellow crystals of $[Zn(OAc)_2(L^3)_{0.5}]$ **7**. The asymmetric unit contains one zinc atom, two acetato ligands and a half of a L^3 , with the spiro carbon atom located on a two-fold axis. The zinc ions are coordinated by four oxygen atoms belonging to the two chelating acetate ligands, one oxygen atom being semicoordinated ($Zn1 - O1 = 2.182(7)$, $Zn1 - O2 = 2.258(9)$, $Zn1 - O3 = 1.930(8)$, $Zn1 - O4 = 2.562(11)$ Å) and two *cis* nitrogen atoms from two ligand molecules ($Zn1 - N1 = 2.054(8)$, $Zn1 - N2^a = 2.043(7)$ Å, $a = 1-x, -1+y, 1.5-z$). Considering the semi-coordination of the oxygen atom, the geometry of zinc centers is distorted octahedral. A neutral 1-D double chain polymer with the same topological features as in **4** and **6** is constructed by reacting zinc acetate and the spirobifluorene derivate L^3 (Figure 7a). The coplanarity of the pyridyl fragments and fluorene units of each tecton branches, in contrast to the case of compound **6** and the free ligand,^[15] promotes the formation of weak off-set π - π stacking contacts between the pyridyl and phenyl ring from adjacent chains (the closest

C $\cdots$ C distances between two rings are 3.59, 3.64 Å). The chains associate in layers with stair-like arrangement through π - π interactions. The neighboring double chains within a supramolecular layer are constituted of metal building blocks with different chiralities (Figure 7b).

Figure 7. (a) Fragment of crystal structure of **7** with the atom numbering scheme (symmetry code: $a = 1-x, -1+y, 1.5-z$); (b) Supramolecular layer constructed from chains bearing metal centres of distinct chiralities (green – delta, violet – lambda configuration).

Selected bond distances and angles for compounds **1–7** are collected in Table 2.

Table 2

The diffuse reflectance spectra of compounds **1–4** have been recorded (Figure S1, S2). The electronic spectrum of compound **2** shows a band with a maximum at 738 nm, characteristic for square pyramidal geometry of Cu^{II} ions. The Co^{II} complexes display similar electronic spectra in agreement with the octahedral stereochemistry of the metal ions and the similarity of the donor atoms: 1130 nm (⁴T₁ → ⁴T₂); 507 nm (⁴T₁ → ⁴T₁(P)) for compound **1**; 1180 nm (⁴T₁ → ⁴T₂); 500 nm (⁴T₁ → ⁴T₁(P)) for compound **4**, assuming the *O* point symmetry group; 1162 nm (⁴T_{1g} → ⁴T_{2g}); 490 nm (⁴T_{1g} → ⁴T_{1g}(P)) for compound **3**.

Magnetic properties

In recent years, Co^{II} based complexes with different coordination geometries have become the focus of intense research aiming at exploiting these systems to obtaining molecular based magnetic memory units.^[16] This is particularly true for all those coordination geometries, such as linear and pseudo-octahedral, where a large unquenched orbital momentum is maintained and a large gap between the ground and first excited doublet is created. This may result in a large easy axis magnetic anisotropy and thus to a barrier to magnetization reversal, with consequent slow relaxation of the magnetization and magnetic bistability at cryogenic temperatures.

A first assessment of the anisotropy of Co^{II} based systems can be performed by measuring the EPR spectrum at low temperature. Indeed, given the semi-integer nature of the spin state of Co^{II} intra-doublet transition within the ground state are almost invariably observed at cryogenic temperatures and can be interpreted on the basis of an effective spin Hamiltonian $\hat{H} = \mu_B \mathbf{B} \cdot \mathbf{g}_{\text{eff}} \cdot \mathbf{S}_{\text{eff}}$.^[17]

The low temperature EPR spectrum of **1**, reported in figure 8 is quite typical for pseudo-octahedral Co^{II} ions and can indeed be interpreted on the basis of an effective anisotropic doublet. In this approach we assume that the exchange interaction between paramagnetic centers is negligible due to the large distance between them and the absence of efficient exchange coupling paths. On the other hand, the absence of the hyperfine structure expected for the interaction of the electronic spins with the *I*=7/2 nuclear spin of ⁵⁹Co indicates that, despite the quite large inter-Co^{II} distances, dipolar interactions and other internal fields are still relevant. The observed spectrum points to an essentially axial system, with *g*_{||} = 6.5 and *g*_⊥ = 2.6 (with only small hints of rhombicity observed). The *g*_{||} > *g*_⊥ condition indicates an easy axis type anisotropy

with relatively large transverse contribution. It is worth noting that such a pattern of g values cannot be accounted for on the basis of a Spin Hamiltonian for an $S=3/2$:

$$H = \mu_B \mathbf{B} \cdot \mathbf{g} \cdot \mathbf{S} + DS_z^2 + E(S_x^2 - S_y^2) \quad (1)$$

where D and E are the axial and rhombic zero field splitting parameters and $\mathbf{g}$ is the real g tensor for an $S=3/2$. Indeed, the relation between real and effective g' values in this case are well known to be the following:

$$g'_1 = g_x \left(1 - \frac{1-3\eta}{\sqrt{1+3\eta^2}}\right), \quad g'_2 = g_y \left(1 - \frac{1+3\eta}{\sqrt{1+3\eta^2}}\right), \quad g'_3 = g_z \left(\frac{2}{\sqrt{1+3\eta^2}} + 1\right) \quad (2)$$

where g_i s are the principal values of $\mathbf{g}$ and η is the rhombicity ratio $0 \leq |E/D| \leq 1/3$.^[18] It follows that to have $g'_1 = g'_2$ by keeping $g_x = g_y$ the only possibility is to have both of them equal to zero. While one can somehow relax the latter condition, it can be easily seen that no reasonable set of parameters is able to reproduce the experimental data. This is consistent with earlier considerations by B. Tsukerblat and coworkers who pointed out that the use of Hamiltonian (1) for negative D is irrelevant to high-spin Co^{II} complex with dominant cubic crystal field and relatively small low-symmetry contributions.^[19]

Figure 8. X-band ($\nu = 9.402$ GHz) EPR spectrum of a microcrystalline powder sample of **1** measured at 5 K. Arrows evidence resonance fields for parallel and perpendicular transitions, respectively. Asterisk marks an unavoidable signal from the cavity.

A more appropriate description, providing also insights about the energetic structure of the Co^{II} center is the one developed by Griffith and later by Figgis^[20] which operates on the ground ⁴T_{1g} term of the octahedral cobalt(II) ion explicitly taking into account the unquenched orbital angular momentum:

$$\mathcal{H} = -\frac{3}{2}\kappa\lambda\hat{L} \cdot \hat{S} + \Delta_{ax} \left[\hat{L}_z^2 - \frac{1}{3}L(L+1) \right] + \mu_B \mathbf{B} \cdot \left(g_s \hat{S} - \frac{3}{2}\kappa\hat{L} \right) \quad (3)$$

The first term of this Hamiltonian describes the spin orbit coupling (SOC) interaction: the orbital reduction parameter (κ) takes into account both the covalence effect and the mixing of ⁴T_{1g}(⁴F) with ⁴T_{1g}(⁴P) due to the crystal field, while $-3/2$ is a constant required by T-P isomorphism.^[21] The second term represents the effect of the distortion from perfect octahedral symmetry due to an axial(tetragonal) crystal field, which splits the orbital triplet ⁴T_{1g} into ⁴A_{2g} ($M_L = 0$) and ⁴E_g ($M_L = \pm 1$). To observe an easy axis type anisotropy of the ground doublet (i.e. a $g_{//} > g_{\perp}$ pattern), a negative value of Δ_{ax} is necessary, resulting in a ground ⁴E_g state which is then split by SOC.^[22] Finally, the third term is the Zeeman interaction, which comprises both spin and orbital contributions. Here, given the essentially axial nature of the observed EPR spectrum, we have neglected the rhombic contribution to the crystal field, notwithstanding the large deviation from tetragonal symmetry of the molecular structure. By fixing the SOC constant to the free ion value ($\lambda = -180 \text{ cm}^{-1}$) the pattern of effective g factors of the ground doublet could be reproduced^[23] using the following parameters: $\Delta_{ax} = -630 \pm 20 \text{ cm}^{-1}$, $\kappa = 0.75 \pm 0.05$. With this set of parameters, the first- and second-excited spin-orbit doublets lie at 220 and 390 cm^{-1} from the ground state.

The same model provides very good reproduction of the isothermal magnetization curves (Figure S3) measured at three different temperatures and a reasonable reproduction of the temperature dependence of the susceptibility (Figure S3 inset), lending support to the proposed energy pattern picture.

The relatively large energy splitting between the first and the second excited state and the easy axis nature of the ground state prompted us to investigate the dynamic magnetic properties of this system. Frequency dependent ac susceptibility data were recorded at the temperature of 2 K evidencing that slow relaxation only occurs on applying an external field (Figure S4): this suggests a large efficiency of Quantum tunnelling processes, which are strongly reduced on field application, in promoting relaxation. The frequency dependent curves are at any rate extremely

broad, suggesting a large dispersion in relaxation times. An investigation as a function of temperature in a field of 200 mT allowed to extract the relaxation times by fitting each isothermal $\chi_M''(\nu)$ plots with a generalized Debye model (best fit parameters are reported in Table S1) which confirmed a broad distribution of relaxation times with α values extremely high especially at low temperature.^[24]

These data are shown as a function of temperature in Figure 9, both as log-log and Arrhenius plot. It is clear that in both cases the curve is deviating from linearity, indicating that more than one process is contributing to the relaxation (pure Orbach would provide linearity in Arrhenius plot, pure Raman in the log-log plot). To reduce the risk of overparametrization we attempted to fit this dependence by two different models. The first one includes a residual Quantum tunnelling, a direct process, and an overbarrier Orbach term: $1/\tau = A_{QT} + B_{dir}T + (\tau_0)^{-1} \exp(-\Delta E/T)$ (where ΔE is the energy difference between the ground state and the excited one through which the systems relaxes); the second one neglects the Orbach term and assumes a Raman process to be active: $1/\tau = A_{QT} + B_{dir}T + C_{Ram}T^9$.^[17]

Figure 9. Temperature dependence of the relaxation rate measured in an applied field of 200 mT as a function of temperature, reported as log-log (right) and Arrhenius plot. Red and blue continuous lines represent the best fit obtained with the two models, including Raman and Orbach term, respectively. See text for more details.

The best fit parameters in the two cases were: $A_{QT} = 1670 \pm 420 \text{ s}^{-1}$, $B_{dir} = 660 \pm 170 \text{ K}^{-1} \text{ s}^{-1}$, $\tau_0 = 4 \pm 4 \times 10^{-6} \text{ s}$, $\Delta E = 35 \pm 15 \text{ K}$ ($R^2 = 0.952$); $A_{QT} = 1760 \pm 213 \text{ s}^{-1}$, $B_{dir} = 640 \pm 74 \text{ K}^{-1} \text{ s}^{-1}$, $C_{Ram} = 1.4 \pm 0.1 \times 10^{-3} \text{ K}^{-9} \text{ s}^{-1}$ ($R^2 = 0.978$). It is to be noted that while the contribution of direct and Quantum tunneling terms are consistent for the two models, the anisotropy barrier derived by including the Orbach term is clearly at odds with the rationalization of the EPR spectrum. At the same time, the energy gap between the ground and first excited doublet in pseudo-octahedral Co(II) is well known to be larger than 70 K, which makes the derived value of ΔE unphysical. Thus, while a conclusive proof about the actual relaxation process would require a detailed spectroscopic and theoretical investigation of the system that is beyond the scope of this paper, it is possible to suggest that, in the investigated temperature range, the relaxation is most likely dominated by a Raman process rather than by an overbarrier Orbach one. We further note that, since EPR spectrum is clearly broadened by dipolar interactions, we cannot rule out the possibility that the observed relaxation is actually due to a collective magnetic mechanism through long range interactions.

Photoluminescent properties

A comparative spectral study for compounds **5**, **7**, L^2 and L^3 was performed (figure 10). The absorption spectra of L^2 (Figure S5) and L^3 (Figure S6) show strong bands at 355 and 315, 335 nm, respectively. No fluorescence emission of L^2 was detected upon excitation at 350 nm while L^3 shows a strong emission band at 425 nm upon excitation at 320 nm (Figure 10a, S7). The diffuse reflectance electronic spectrum of **5** exhibits two bands with λ_{max} at 222 and 320 nm. Compound **5** emits a blue fluorescence at $\lambda_{max} = 402 \text{ nm}$ when excited at 350 nm (Figure 10b). The absorption spectrum of **7** displays two broad bands (λ_{max} at 370 and 393 nm). Upon excitation at 370 nm, compound **7** exhibits blue luminescence with emission band maximum at 483 nm and a low intensity shoulder at lower energy (512 nm) (Figure 10c). The emission of **7** is considerably more intense and red-shifted in comparison with that of the free ligand. The blue emission of compound **7** originates from the $\pi^*-\pi$ transitions of the metal perturbed ligand.

Figure 10. (a) Solid state emission spectrum for L^3 ; (b) Absorption (blue) and emission (red) spectra of compound **5**; (c) Absorption (blue) and emission (red) spectra of compound **7**.

Conclusions

Six new coordination polymers and a dinuclear complex were synthesized and characterized using organic linkers constructed on tetrahedral or tetragonal cores decorated with cyano or pyridyl fragments. The structural diversity of the compounds arises from the different stereochemical preferences of the metal ions and the potential of the organic tectons to act either as bidentate or tetradentate bridges between metal centers. The spatial orientation of the available coordination sites in the assembling metal species plays a key role in fashioning the network topologies. Compound **1** is a two-fold interpenetrated 2-D coordination polymer featuring a grid topology. The low dimensionality of compound **1** is attributed to the *cis*-arrangement of nitrogen donor atoms in the $\{Co(hfac)_2N_2\}$ units, in contrast to the expected 3-D net of the *trans* coordination of the ligand donor atoms to the metal centre. Two different topological structures

have been constructed from the same ligand and metal building blocks displaying either *trans* or *cis* configurations. The assembling of spiro based orthogonal platforms and *cis* configured metal centers promoted the formation of diamond chains. Compound **1** was characterized from magnetic point of view. It shows slow relaxation of the magnetization arising most likely from a Raman process. The photoluminescent properties of **5** and **7** shows a solid state emission at $\lambda_{\text{max}} = 402$ and 483 nm, respectively.

Experimental Section

Materials

All reagents and solvents, purchased from commercial sources, were used as received, without further purification.

(L^1)^[6d], (L^2)^[11e] and (L^3)^[15] were synthesized as previously described.

IR spectra (KBr pellets) were recorded on a Bruker Tensor 37 spectrophotometer in 4000 to 400 cm^{-1} frequencies range. Diffuse reflectance spectra were performed on a JASCO V-670 spectrophotometer, using MgO as a standard. X-ray powder diffraction data were recorded on Proto diffractometer at 298 K. Elemental analysis was carried out on a EuroEa Elemental Analyser. Thermogravimetric analysis was performed on a Perkin Elmer STA-600 thermal analyzer in nitrogen atmosphere. The heating rate was $10^\circ\text{C min}^{-1}$ from room temperature from 30 to 400°C .

The fluorescence spectra were carried out on a JASCO FP-6500 (**5**) and JASCO FP-8300 (L^3 , **7**) spectrofluorimeters.

X-band EPR spectrum was recorded on a polycrystalline sample using an Elecsys E500 EPR spectrometer (Bruker GmbH) equipped with a SHQ cavity and a continuous ^4He flow ESR900 cryostat (Oxford instrument) to work at low temperature. Ac susceptibility data were measured using a Quantum Design PPMS (Physical Property measurementsystem), equipped with an ac susceptometer insert.

Crystallographic data collection and structure determination

Single crystals X-ray measurements were performed on a SuperNova, Dual, Cu at zero, Eos (compounds **2**), a Xcalibur, Eos diffractometer (compound **4**) and on a STOE IPDS II single crystal diffractometer, using graphite-monochromated Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$)

(compounds **1**, **3**, **5-7**). The structures were solved by direct methods and refined by full-matrix least-squares techniques based on F^2 using the SHELXL-2013 program package.^[25] The non-H atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in fixed, idealized positions and refined as rigidly bonded to the corresponding carbon atoms. Crystallographic data and structure refinement parameters for **1-7** are presented in Table 1. CCDC reference numbers for crystals **1-7**: 1906053 – 1906059; **5a**: 1959258.

Table 1

Synthesis of $[\text{Co}(\text{hfac})_2(\text{L}^1)_{0.5}]$ **1**: $[\text{Co}(\text{hfac})_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ (0.0029 g, 0.0059 mmol) was solubilized in 4 mL boiling *n*-heptane. Upon cooling to room temperature, 4 mL of CH_2Cl_2 were added and the solution was carefully layered on top of 2 mL CH_2Cl_2 solution of L^1 (0.0016 g, 0.0029 mmol) in a test tube. Red single crystals were formed in few days. Selected IR data (KBr, cm^{-1}): 2955(w), 2932(w), 2861(w), 2269(m), 1643(s), 1607(m), 1552(m), 1523(m), 1486(m), 1406(w), 1355(w), 1252(vs), 1197(vs), 1150(vs), 1099(m), 834(m), 792(m), 743(w), 669(m), 582(w). Elemental analysis calcd for $\text{C}_{29}\text{H}_{16}\text{CoF}_{12}\text{N}_2\text{O}_4$: C, 46.86; H, 2.17; N, 3.77 %. Found: C, 46.44; H, 2.28; N, 3.76 %. UV-Vis: 310, 347, 470, 507, 1130 nm.

Synthesis of $[\text{Cu}_2(\text{hfac})_4\text{L}^2]$ **2**: $[\text{Cu}(\text{hfac})_2\text{H}_2\text{O}] 2\text{H}_2\text{O}$ (0.004 g, 0.008 mmol) was solubilized in 4 mL boiling *n*-heptane. After cooling to room temperature, 2 mL of CH_2Cl_2 solution of L^2 (0.0017 g, 0.004 mmol) were added, and the mixture was stirred for 10 minutes. Green single crystals were formed by slow evaporation of the solvent in few days. Selected IR data (KBr, cm^{-1}): 2965(w), 2938(w), 2858(w), 2362(m), 2347(m), 2254(m), 2230(m), 1639(s), 1610(m), 1561(m), 1534(m), 1471(s), 1414(w), 1354(w), 1255(vs), 1215(vs), 1149(vs), 1106(m), 871(w), 832(m), 805(m), 746(w), 680(m), 594 (w). Elemental analysis calcd for $\text{C}_{49}\text{H}_{16}\text{Cu}_2\text{F}_{24}\text{N}_4\text{O}_8$: C, 42.90; H, 1.18; N, 4.08 %. Found: C, 42.37; H, 1.19; N, 4.26 %. UV-Vis: 321, 440, 738 nm.

Synthesis of $[\text{Co}(\text{hfac})_2\text{L}^2]$ **3**: $[\text{Co}(\text{hfac})_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ (0.0056 g, 0.0113 mmol) was solubilized in 4 mL boiling *n*-heptane. Upon cooling to room temperature, 2 mL of CH_2Cl_2 and 2 mL of MeOH were added and the solution was carefully layered on top of 4 mL CH_2Cl_2 solution of L^2 (0.0024 g, 0.0057 mmol) in a test tube. Orange single crystals were formed in few days. Selected IR data (KBr, cm^{-1}): 2972(w), 2919(w), 2851(w), 2381(m), 2289(m), 2223(s), 1605(s), 1579(m),

1465(s), 1412(m), 1338(w), 1266(w), 1208(m), 1120(s), 1047(m), 1005(m), 970(m), 884(m), 854(s), 828(m), 772(m), 655(m), 564(w). Elemental analysis calcd for $C_{39}H_{14}CoF_{12}N_4O_4$: C, 52.66; H, 1.59; N, 6.30 %. Found: C, 53.16; H, 1.19; N, 6.02 %. UV-Vis: 321, 421, 490, 1162 nm.

Synthesis of $[Co(hfac)_2(L^2)_{0.5}] \cdot 8H_2O$ **4**: $[Co(hfac)_2(H_2O)_2] \cdot H_2O$ (0.007 g, 0.0142 mmol) was solubilized in 4 mL boiling *n*-heptane. Upon cooling to room temperature, 4 mL of CH_2Cl_2 solution of L^2 (0.0019 g, 0.0045 mmol) were added and the mixture was stirred for 10 minutes. To the blurry red pale solution were add 2 mL of MeOH and left to slowly evaporate. Dark red single crystals were formed in few days. Selected IR data (KBr, cm^{-1}): 2968(w), 2934(w), 2365(m), 2343(m), 2268(m), 1644(s), 1555(m), 1526(m), 1495(m), 1415(w), 1346(w), 1259(vs), 1206(vs), 1147(vs), 1100(m), 892(w), 831(m), 793(m), 761(w), 669(m), 585(w). Elemental analysis calcd for $C_{49}H_{48}Co_2F_{24}N_4O_{24}$: C, 35.65; H, 2.93; N, 3.39 %. Found: C, 35.9; H, 2.91; N, 3.43 %. UV-Vis: 310, 420, 500, 1180 nm

Synthesis of $[AgL^2](SbF_6) \cdot CH_3COOC_2H_5$ **5**: An ethylacetate solution (2 mL) of $AgSbF_6$ (0.002g, 0.0058 mmol) was left to slowly diffuse through a 2 mL layer of ethylacetate and dichloromethane (1:1 v/v) into a solution of 0.0025g (0.006 mmol) L^2 dissolved in 2 mL CH_2Cl_2 . Colorless single crystals were formed in few days. Selected IR data (KBr, cm^{-1}): 2923(w), 2853(w), 2246(s), 1730(s), 1608(s), 1464(s), 1414(m), 1247(m), 1208(m), 1148(m), 1110(m), 1041(m), 879(w), 821(w), 775(w), 658(s), 566(s). Elemental analysis calcd for $C_{33}H_{20}AgF_6N_4O_2Sb$: C, 46.73; H, 2.38; N, 6.61 %. Found: C, 46.04; H, 2.82; N, 6.78 %.

Synthesis of $[AgL^2](SbF_6)$ **5a**: Colorless single crystals of **5a** were obtained from single crystals of **5** by heating at 90°C for 48h, through the single-crystal-to-single-crystal transformation.

Synthesis of $[Mn(hfac)_2(L^3)_{0.5}]$ **6**: An ethanol solution (4 mL) of $[Mn(hfac)_2(H_2O)_2] \cdot H_2O$ (0.0053g, 0.0101 mmol) was left to slowly diffuse through a 5 mL layer of ethanol and into a solution of 0.0016 g (0.0025 mmol) L^3 dissolved in 4 mL $CHCl_3$. Yellow single crystals were formed after the slow evaporation in few days. Selected IR data (KBr, cm^{-1}): 2964(m), 2906(w), 1649(m), 1611(m), 1555(w), 1493(m), 1414(w), 1261(vs), 1195(s), 1096(vs), 1020(vs), 800(vs),

663(m), 581(w). Elemental analysis calcd for $C_{65}H_{32}Mn_2F_{24}N_4O_8$: C, 49.95; H, 2.06; N, 3.59 %. Found: C, 50.03; H 2.05; N, 3.14 %.

Synthesis of $[Zn(OAc)_2(L^3)_{0.5}]$ **7**: A solution of $Zn(OAc)_2 \cdot H_2O$ (0.0028g, 0.012 mmol) in 4 ml MeOH was added to a solution of 0.002 g (0.0032 mmol) L^3 dissolved in 4 mL DMF and 2 mL MeOH. After two hours of stirring, the mixture was filtered and left in air to slowly evaporate. Yellow single crystals were formed in two weeks. Selected IR data (KBr, cm^{-1}): 29642(m), 2918(s), 2850(m), 1613(s), 1611(m), 1433(s), 1384(vs), 1261(s), 1097(s), 1025(vs), 981(vs), 905(s), 803(s), 708(m). Elemental analysis calcd for $C_{53}H_{40}Zn_2N_4O_8$: C, 64.19; H, 4.07; N, 5.65 %. Found: C, 64.03; H, 4.28; N, 5.19 %.

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Table 1

	1	2	3	4	5	5a	6	7
Formula sum	C ₂₉ H ₁₆ Co ₁ F ₁₂ N ₂ O ₄	C ₄₉ H ₁₆ Cu ₂ F ₂₄ N ₄ O ₈	C ₃₉ H ₁₄ Co ₁ F ₁₂ N ₄ O ₄	C _{24.5} H ₂₄ Co ₁ F ₁₂ N ₂ O ₁₂	C ₃₃ H ₂₀ Ag ₁ F ₆ N ₄ O ₂ Sb ₁	C ₂₉ H ₁₂ Ag ₁ F ₆ N ₄ Sb ₁	C _{32.5} H ₁₆ Mn ₁ F ₁₂ N ₂ O ₄	C ₅₃ H ₄₀ Zn ₂ N ₄ O ₈
Formula weight	743.37	1371.74	889.47	825.95	848.15	760.05	781.41	991.63
Crystal system	tetragonal	monoclinic	Triclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	<i>I</i> ₄ /a	<i>P</i> 2 ₁ /c	<i>P</i> -1	<i>C</i> 2/c	<i>P</i> 2 ₁ /n	<i>P</i> 2 ₁ /n	<i>C</i> 2/c	<i>P</i> 2/c
<i>a</i> /Å	11.507(5)	12.4464(9)	9.2750(13)	23.909(3)	10.737(2)	10.600(7)	27.741(4)	10.5822(6)
<i>b</i> /Å	11.507(5)	18.3505(9)	14.767(2)	12.654(3)	11.414(2)	11.2419(5)	14.9519(16)	13.4700(7)
<i>c</i> /Å	52.357(4)	24.3918(18)	15.708(3)	22.403(3)	27.106(4)	26.370(2)	19.146(3)	20.8256(13)
α /°	90.000	90.000	103.954(12)	90.000	90.000	90.000	90.000	90.000
β /°	90.000	102.981(7)	98.248(12)	114.278(17)	97.267(13)	98.029(6)	123.579(10)	93.011(5)
γ /°	90.000	90.000	99.424(11)	90.000	90.000	90.000	90.000	90.000
V/Å ³	6932.6(8)	5428.7(6)	2021.8(5)	6178.5	3295.5(8)	3187.9(4)	6616.2(2)	2964.4(3)
Z	8	4	2	8	4	4	4	2
<i>D</i> _c /g cm ⁻³	1.424	1.678	1.461	1.571	1.709	1.584	1.569	1.111
T/K	150(2)	293(2)	293(2)	199.9(1)	293	293	293(2)	293(2)
μ /mm ⁻¹	0.593	0.922	0.524	0.670	1.484	1.519	0.507	0.856
Reflections collected	14866	28029	23288	10440	37665	27390	24100	34955
Independent	3066	9561	7089	5045	5802	5541	5686	5224
reflection	[<i>R</i> _{int} = 0.2355]	[<i>R</i> _{int} = 0.0505]	[<i>R</i> _{int} = 0.1201]	[<i>R</i> _{int} = 0.0672]	[<i>R</i> _{int} = 0.1558]	[<i>R</i> _{int} = 0.0983]	[<i>R</i> _{int} = 0.0581]	[<i>R</i> _{int} = 0.1513]
<i>R</i> _{<i>I</i>} ^{<i>a</i>} [<i>I</i> > 2σ(<i>I</i>)]	0.0799	0.0839	0.0656	0.0999	0.0549	0.0873	0.0545	0.0914
<i>wR</i> ₂ ^{<i>b</i>} (all data)	0.2490	0.2361	0.1750	0.2939	0.1545	0.3087	0.1556	0.3413
GOF	1.009	1.015	0.959	0.953	0.871	1.041	0.802	1.008
$\Delta\rho_{\min}/\Delta\rho_{\max}$ (e Å ⁻³)	-0.48/ 0.46	-0.62/0.75	-0.60/ 0.60	-0.55/0.84	-0.86/ 0.53	-0.83/ 1.22	-0.38/ 0.43	-0.40/0.53

$$^a R_I = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}; \quad w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP] \quad \text{where } P = [\max(F_o^2, 0) + 2F_c^2] / 3.$$

Table 2

1		2		3		4		5		5a		6		7	
Co1–O1	2.082(6)	Cu1 – O1	1.946(4)	Co1–O1	2.053(4)	Co1–O1	2.074(7)	Ag1–N1	2.287(7)	Ag1–N1	2.253(14)	Mn1 – O1	2.193(3)	Zn1–O1	2.182(7)
Co1–O2	2.045(6)	Cu1 – O2	1.926(4)	Co1–O2	2.053(4)	Co1–O2	2.024(8)	Ag1–N2 ^a	2.259(7)	Ag1–N2 ^a	2.260(14)	Mn1 – O2	2.155(4)	Zn1–O2	2.258(9)
Co1–N1	2.116(8)	Cu1 – O3	1.940(4)	Co1 –O3	2.034(5)	Co1 –O3	2.062(9)	Ag1–N3 ^b	2.247(7)	Ag1–N3 ^b	2.244(15)	Mn1 – O3	2.144(4)	Zn1 –O3	1.930(8)
		Cu1 – O4	1.928(4)	Co1 –O4	2.050(4)	Co1 –O4	2.031(7)	Ag1–N4 ^c	2.297(7)	Ag1–N4 ^c	2.301(16)	Mn1 – O4	2.195(3)	Zn1 –O4	2.562(11)
		Cu1 – N4	2.270(6)	Co1–N1	2.118(4)	Co1–N1	2.177(10)					Mn1 – N1	2.233(4)	Zn1–N1	2.054(8)
		Cu2 – O5	1.938(5)	Co1–N2 ^a	2.128(4)	Co1–N2	2.089(10)					Mn1 – N2 ^a	2.243(4)	Zn1–N2 ^a	2.043(7)
		Cu2 – O6	1.947(5)												
		Cu2 – O7	1.925(5)												
		Cu2 – O8	1.947(5)												
		Cu2 – N1	2.266(6)												
O1 Co1 O2	87.5(2)	O1 Cu1 O2	91.2(2)	O1 Co1 O2	88.3(2)	O1 Co1 O2	88.1(3)	N1 Ag1 N2 ^a	117.9(3)	N1 Ag1 N2 ^a	118.7(6)	O1 Mn1 O2	81.7(2)	O1 Zn1 O2	57.5(3)
O1 Co1 O1 ^a	87.5(3)	O1 Cu1 O3	175.2(2)	O1 Co1 O3	91.7(3)	O1 Co1 O3	87.9(3)	N1 Ag1 N3 ^b	112.2(3)	N1 Ag1 N3 ^b	110.2(7)	O1 Mn1 O3	96.3(1)	O1 Zn1 O3	118.5(4)
O1 Co1 O2 ^a	93.5(2)	O1 Cu1 O4	87.8(2)	O1 Co1 O4	178.4(2)	O1 Co1 O4	96.6(3)	N1 Ag1 N4 ^c	98.7(3)	N1 Ag1 N4 ^c	98.1(7)	O1 Mn1 O4	79.3(1)	O1 Zn1 O4	168.6(3)
O1 Co1 N1	90.3(3)	O1 Cu1 N4	90.8(2)	O1 Co1 N1	90.3(2)	O1 Co1 N1	179.4(3)	N2 ^a Ag1 N3 ^b	102.9(3)	N2 ^a Ag1 N3 ^b	103.5(7)	O1 Mn1 N1	95.2(2)	O1 Zn1 N1	90.5(3)
O1 Co1 N1 ^a	177.6(3)	O2 Cu1 O3	87.7(2)	O1 Co1 N2 ^a	88.9(2)	O1 Co1 N2	90.3(3)	N2 ^a Ag1 N4 ^c	109.2(3)	N2 ^a Ag1 N4 ^c	112.0(7)	O1 Mn1 N2 ^a	164.9(2)	O1 Zn1 N2 ^a	101.7(3)
O2 Co1 O2 ^a	178.7(3)	O2 Cu1 O4	168.6(2)	O2 Co1 O3	178.7(2)	O2 Co1 O3	91.7(4)	N3 ^b Ag1 N4 ^c	116.6(3)	N3 ^b Ag1 N4 ^c	114.8(7)	O2 Mn1 O3	177.0(2)	O2 Zn1 O3	91.8(4)
O2 Co1 O1 ^a	93.5(2)	O2 Cu1 N4	95.2(2)	O2 Co1 O4	91.4(2)	O2 Co1 O4	175.0(3)					O2 Mn1 O4	94.9(2)	O2 Zn1 O4	116.3(3)
O2 Co1 N1	87.2(3)	O3 Cu1 O4	92.2(2)	O2 Co1 N1	86.5(2)	O2 Co1 N1	91.8(4)					O2 Mn1 N1	94.8(2)	O2 Zn1 N1	147.7(3)
O2 Co1 N1 ^a	91.9(3)	O3 Cu1 N4	94.0(2)	O2 Co1 N2 ^a	88.9(2)	O2 Co1 N2	93.2(4)					O2 Mn1 N2 ^a	85.1(2)	O2 Zn1 N2 ^a	94.3(3)
O1 ^a Co1 O2 ^a	87.5(2)	O4 Cu1 N4	96.2(2)	O3 Co1 O4	88.5(2)	O3 Co1 O4	87.0(3)					O3 Mn1 O4	82.5(1)	O3 Zn1 O4	50.4(3)
O1 ^a Co1 N1	177.6(3)	O5 Cu2 O6	92.1(2)	O3 Co1 N1	94.7(2)	O3 Co1 N1	91.6(3)					O3 Mn1 N1	87.4(2)	O3 Zn1 N1	101.0(4)
O1 ^a Co1 N1 ^a	90.3(3)	O5 Cu2 O7	163.0(2)	O3 Co1 N2 ^a	89.8(2)	O3 Co1 N2	174.7(4)					O3 Mn1 N2 ^a	96.4(2)	O3 Zn1 N2 ^a	135.4(4)
O2 ^a Co1 N1	91.9(3)	O5 Cu2 O8	87.3(2)	O4 Co1 N1	88.1(3)	O4 Co1 N1	83.5(3)					O4 Mn1 N1	167.9(2)	O4 Zn1 N1	94.3(3)
O2 ^a Co1 N1 ^a	87.2(3)	O5 Cu2 N1	92.4(2)	O4 Co1 N2 ^a	92.5(3)	O4 Co1 N2	88.3(4)					O4 Mn1 N2 ^a	94.5(2)	O4 Zn1 N2 ^a	87.8(3)

N1 Co1 N1 ^a 92.0(4)	O6 Cu2 O7 87.2(2)	N1 Co1 N2 ^a 175.4(2)	N1 Co1 N2 90.3(3)	N1 Mn1 N2 ^a 93.1(2)	N1 Zn1 N2 ^a 96.8(3)
	O6 Cu2 O8 176.8(2)				
	O6 Cu2 N1 92.6(2)				
	O7 Cu2 O8 92.4(2)				
	O7 Cu2 N1 104.6(2)				
	O8 Cu2 N1 90.6(2)				
^a = 1-x, 0.5-y, z	^a = -1+x, -1+y, z	^a = -1+x, -1+y, z ^b = x, -1+y, z ^c = -1+x, y, z	^a = -1+x, -1+y, z ^b = x, -1+y, z ^c = -1+x, y, z	^a = x, -1+y, z	^a = 1-x, -1+y, 1.5-z

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Structural diversity ranging from oligonuclear complexes to 1-D and 2-D coordination polymers generated by tetrasubstituted adamantane and spirobifluorene derivatives

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Adamantane and spirobifluorene functionalized with coordinating groups are employed as ligands against various metal ions (Ag^+ , Zn^{2+} , Co^{2+} , and Mn^{2+}), resulting in oligonuclear and coordination polymers.

Keywords: coordination polymers; tetradentate spacers, magnetic properties; luminescent properties; single-crystal-to-single-crystal processes

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