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Dedicated to the memory of
Professor Mircea D. Banciu (1941–2005)

RACK, SQUARE AND DOUBLE HELICAL DINUCLEAR METALLOSUPRAMOLECULAR ARCHITECTURES – COORDINATION BEHAVIOR, ANION BINDING AND STACKING INTERACTIONS

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We describe here a study of the coordination binding of Co^{2+}, Cu^{2+} and Pb^{2+} ions to the ditopic ligand **1**, leading to the formation of rack-type and double helical monomers. We report the crystal structures of three such complexes **5**-**7**, which further self-organize into complementary duplex-rack, square and double helical architectures in the solid state. The ligand **1** discussed in this paper operates under conditions in which the two terpyridine (terpy) coordination sites resulted from Pyridine-Pyridine-Pyridazine connected sequences can be involved in the orthogonal binding events of the octahedral metal ions. In terms of molecular adaptability the formation of rack-type and double helical architectures represents the best coordination frameworks of the rigid ligand **1** presenting unfavorable orientation of coordination vectors. In terms of programmed self-assembly the formation of the different metallo-architectures **5, 6** and **7** underlines the fact that, despite the role of the strength of the coordination interactions and of maximal site occupation, other factors like stacking, binding of anions (triflate or tetrafluoroborate anions stabilizing the network of metallic ions) and of solvent molecules may interfere and influence the nature of the favored output species.

INTRODUCTION

The spontaneous but controlled generation of functional supramolecular architectures by self-assembly has emerged as a major development of supramolecular chemistry toward the design of self-organizing systems of increasing complexity.[1] In particular, the self-assembly of inorganic supramolecular entities is based on the implementation of ligands containing specific molecular information stored in the arrangement of suitable binding sites and of metal ions reading out the structural information through the algorithm defined by their coordination geometry.[1,2] Of special interest among the great variety of possible superstructures are those in which metals ions are structured in a rack[3], grid[4] or double helical architectures[5], which present intriguing features as multisite species of interest for nanotechnology, as eventual components of information storage devices. The formation structure and stability of such coordination networks gives access to a variety of supramolecular architectures, incorporating different arrays of metal ions, of precisely defined position and nuclearity, which may be expected to exhibit a wide variety of physicochemical properties. [3-5]

We describe here our results on the species formed by metal ion coordination with the ditopic ligand **1** which presents two terpyridine (terpy) type coordination subunits (Scheme 1). The coordinate vectors of ligand **1** in complexed form converge inward at an angle of approximately 80° in an idealized geometry. The coordinate vectors[6] (Scheme 1) of a similar ligand **2** usually leading to grid complexes, lie naturally parallel.[7] Examples of grid architectures in which coordinate vectors converge outward (~60°)[8a] or inward (~60°)[8b]

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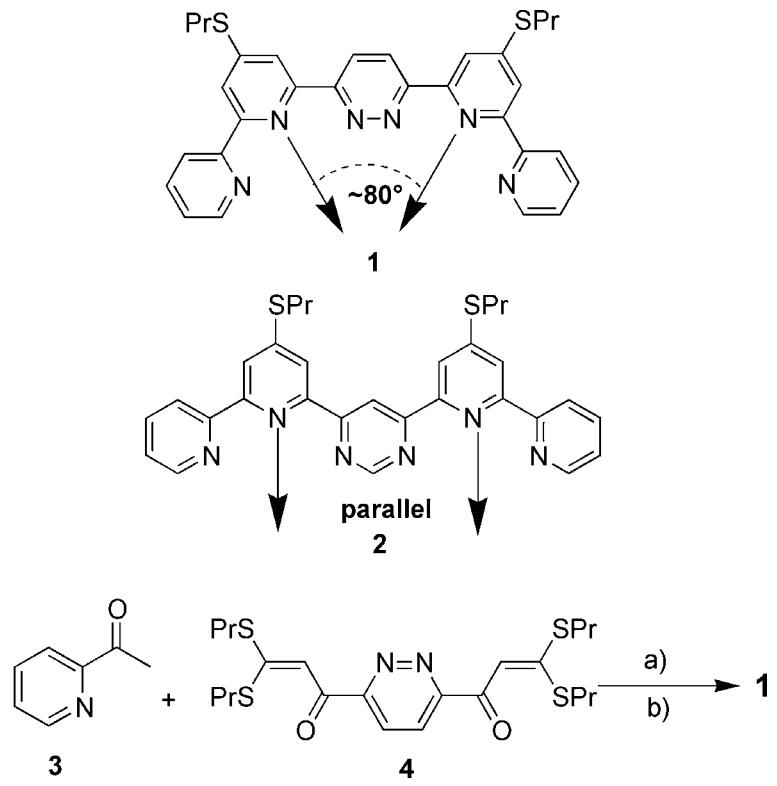
have recently been reported, these architectures present distorted coordination geometries and are stabilized by supplementary hydrophobic interactions.



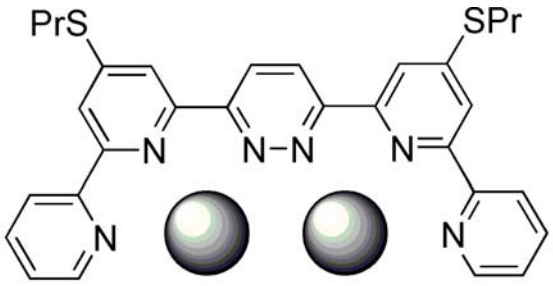
Scheme 1: The coordinate vectors[6] of ligands **1** and **2** and reaction sequence for the preparation of ligand **1**: a) *t*BuOK, THF; b) AcOH/NH_4OAc, reflux.

Specifically, we investigated the nature of the metallosupramolecular architectures resulting from the combination of different octahedral metal ions with the ligand **1**. We describe here a study of the binding of Co^{2+}, Cu^{2+} and Pb^{2+} metal ions to ligand **1**, leading to the formation of rack-type and double helical monomers. We report the crystal structures of three such complexes **5**-**7**, which further self-organize into complementary duplex-rack, square-rack and double helical metallosupramolecular architectures in the solid state.

RESULTS AND DISCUSSION

Synthesis of ligand 1: Alternating pyridine-pyridazine (Py-Pyz) strands comprising up to thirteen heterocycles and folding into multi-turn helical structures[7] were previously reported by our group. The ligand **1** was first isolated as a side-product in the synthesis of more extended ligands.[7] We report now its direct synthesis using a Potts' methodology[9] along a direct strategy developed earlier[4e]: repetitive twofold reaction of the bifunctional central pyridazine bis-Michael acceptor unit **4**[7] with two acetylpyridine building blocks **3** yields **1** (71.6%).

Generation of the Co^{2+}, Cu^{2+} and Pb^{2+} Complexes of the Ligand 1: The ability of a ligand such as **1** to form different metal complexes gives access to a diverse set of arrays of metal ions. We investigated the formation and existence domain of dinuclear complexes that may result from the binding of Co^{2+} , of Cu^{2+} and of Pb^{2+} ions to 1:1 and 2:1 ratios of ligand **1**. Such systems form by self-assembly under mild conditions and are readily amenable to solution studies by ESI mass spectrometry. The addition of $Co(BF_4)_2$, $Cu(CF_3SO_3)_2$ or $Pb(CF_3SO_3)_2$ to an acetonitrile suspension of **1** caused a rapid dissolution of the ligand. At 1: 1 and 2 : 1, M^{2+} : **1** ratios the ESI spectra were consistent with the presence of the $[\mathbf{1}Co_2]^{4+}$, **5**, $[\mathbf{1}Cu_2OH]^{3+}$, **6** and $[\mathbf{1}_2Pb_2]^{4+}$, **7**, dinuclear complexes.



5=$[\mathbf{1}Co_2]^{4+}$, **6**= $[\mathbf{1}Cu_2OH]^{3+}$, **7**=$[\mathbf{1}_2Pb2]^{4+}$

The ESI mass spectrometry results allow the following conclusions to be drawn :

Anticipating the crystal structure below, the mass spectroscopic data agree with the formation in acetonitrile solution of dinuclear rack-type structures **5**, **6** and of the duplex structure **7** and not of the grid-type structures, of 1 : 1 stoechiometry.

The rack-type duplex **5**, **6** and the duplex structure **7** are highly robust as they are observed even at 1 : 1 ratios, despite the presence of several unoccupied ion binding sites.

Solid state structures of the dinuclear Co^{2+}, Cu^{2+} and Pb^{2+} complexes 5, 6, 7 formed by ligand 1: The crystal structures of the complexes $\mathbf{1}Co^{2+}{}_2$, **5**, $\mathbf{1}Cu^{2+}{}_2(OH)$, **6**, and $\mathbf{1}_2Pb^{2+}{}_2$, **7** formed by ligand **1** with Co^{2+}, Cu^{2+} or Pb^{2+} metal ions, were determined from crystals obtained from 1/5, v/v acetonitrile/ benzene (**5**), nitromethane/benzene (**6**) and acetonitrile/*i*-propylether, (**7**) solutions respectively at room temperature.

The unit cell of **5** was found to contain four $[\mathbf{1}Co^{2+}{}_2]$ rack-type complexes, together with eight tetrafluoroborate counterions, ten acetonitrile, two water and four benzene molecules. The molecular and the crystal packing structures are presented in Figure 1.

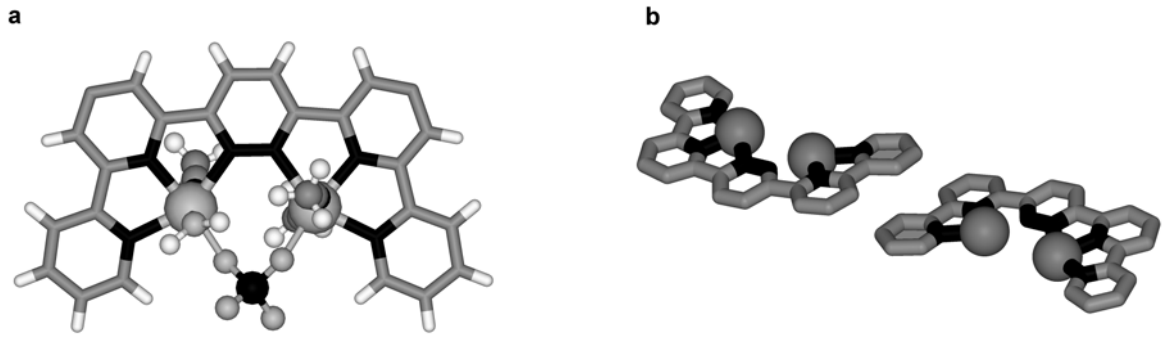


Fig. 1 – Crystal structure of the rack-type complex $[\mathbf{1}Co^{2+}{}_2]$, **5**: a) side view in stick representation; b) stick representation of the crystal packing. The Co^{2+} ions are shown as gray spheres. The BF_4^-, acetonitrile and water molecules are in ball and stick representation. The S*n*Pr groups have been omitted for clarity.

The Co^{2+} metal ions present an octahedral coordination geometry and are coordinated each by one terpy unit: the Co^{2+}-N distances are 2.15 Å (terminal pyridine) 2.04 Å (central pyridine) and 2.25 Å (pyridazine), respectively. The open faces of the metal ions are not identically coordinated; they are occupied by two acetonitrile molecules (the average Co^{2+}-NCAc distance is 2.11 Å) for one Co^{2+} ion and by one acetonitrile and one water molecules for the other one (the Co^{2+}-OH_2 distance is 2.14 Å), respectively (Figure 1a). The position of one BF_4^- counterion is very unusual and deserves some comment. As shown in Figure 1a, the BF_4^- anion undergoes bidentate binding through one fluorine with each cationic center, thus filling the sixth coordination site of the two Co^{2+} ions (the average Co^{2+}-F distance is 2.01 Å). It furthermore presents OH_w···F and two C-H···F hydrogen-bond interactions (average H-F distance of 2.75 Å). The other seven BF_4^- counterions and the solvent molecules are situated in close proximity to the cationic complex. The rack-type complexes **5** associate two by two in the crystal lattice by terminal pyridine-pyridine offset-face-to-face (*off*)[10a] interactions (π-π stacking centroid-centroid distances of 3.98 Å), resulting in the

formation of dimers which are alternatively stratified in the parallel layers in the crystal lattice (Figure 1b). The unit cell of **6** was found to contain four [**1**Cu^{2+}_2OH] complexes, together with six triflate counterions and two nitromethane molecules. The molecular and the crystal packing structures are presented in Figure 2. The Cu^{2+} metal ions present a five-coordinate geometry and are bound each to one terpy unit: the average Cu^{2+}-N distances is 1.95 Å. Two triflate (average Cu-OTf distance ~2.45 Å) and one OH^- (Cu-OH distance ~1.86 Å) counterions are located as coordinating bridges between the two adjacent copper ions (Figure 2a). Additional four triflate counterions and solvent molecules are situated in close proximity to the cationic complex so that all available void space between ligands is filled. In the crystal the two [**1**Cu^{2+}_2OH] complexes form a dimeric self-complementary molecular square (Figure 2b), each [**1**M^{2+}] entity overlapping with the other through π-π interactions between the terminal pyridines (π-π stacking centroid-centroid distances of 3.65 Å).

Each square-type duplex of **6** associate four by four in the crystal lattice by bipyridine- bipyridine *off* [10a] lateral interactions (π-π stacking centroid-centroid distances of 3.65 Å), resulting in the formation of parallel layers which are alternately stratified above each other in a ABAB arrangement such that the outer edges of the squares of each layer overlap markedly (Figure 2c,d).

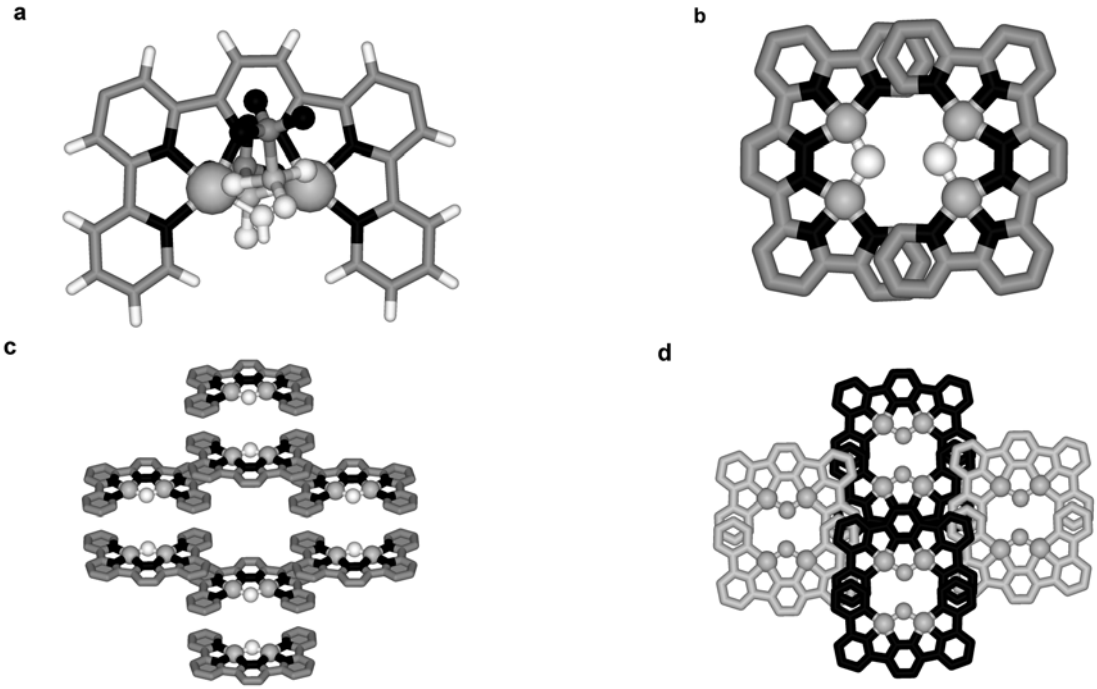


Fig. 2 – Crystal structure of the square-type complex [**1**Cu^{2+}_2(OH)]$_2$ **6**: stick representation of a) side view of the monomer; b) square-type dimmers; c) side view and d) top view of the crystal packing. The Cu^{2+} ions are shown as gray spheres. The $CF_3SO_3^-$ and hydroxide counterions are in ball and stick representation. The S*n*Pr groups have been omitted for clarity.

The unit cell of **7** was found to contain four **1**$_2Pb^{2+}_2$ complexes, together with eight triflate counterions, two *i*-propylether and twelve acetonitrile molecules. The molecular and the crystal packing structures are presented in Figure 3. Both ligands are fully coordinated through all of their nitrogen sites to the Pb^{2+} ions; they are wrapped, displaying a *cisoid* conformation around all inter-heterocyclic C–C bonds (Figure 3a, b). The coordination polyhedron around the lead ions reveals a hemidirected structure[11] and all Pb^{2+} ions present a distorted eight-coordinate geometry. The average Pb-N distances are 2.47 Å (terminal pyridine), 2.60 Å (central pyridine) and 2.70 Å (pyridazine). The open faces of the metal ions are oriented towards the interior of the double helix and are occupied each by two internally coordinated triflate counterions (average Pb-O distance ~2.75 Å), located as coordinating bridges between two adjacent lead atoms. The external triflate counterions and the solvent molecules fill the interstices between the cations, so that all available void space between the double helical entities is filled. The average distance of the Pb^{2+} ions of 3.89 Å is very close than the sum of their ionic radii (about 3.86 Å), indicating a Pb^{2+}- Pb^{2+} contact, dictated by ligand packing. In the

crystal, each duplex of one helical sense is π-π stacked with two duplexes of the opposite helical sense (Figure 3c,d). In the crystal lattice the double helical cations pack asymmetrically into parallel layers. On one side, they are alternately slotted into the other in a ABAB arrangement, presenting a tight contact with the two neighboring ones by stacking one set of the terminal Py (centroid-centroid distance of about 3.42 Å) and of the central Py (centroid-centroid distance of about 3.79 Å). On the other side, the outer edges of each layer are in van der Waals contact (Figure 3e). This pattern generates an asymmetric ovoidal "egg" shape for the double-helix duplex (Figure 3d), the ligands presenting a compact arrangement on the slotted stacked periphery.

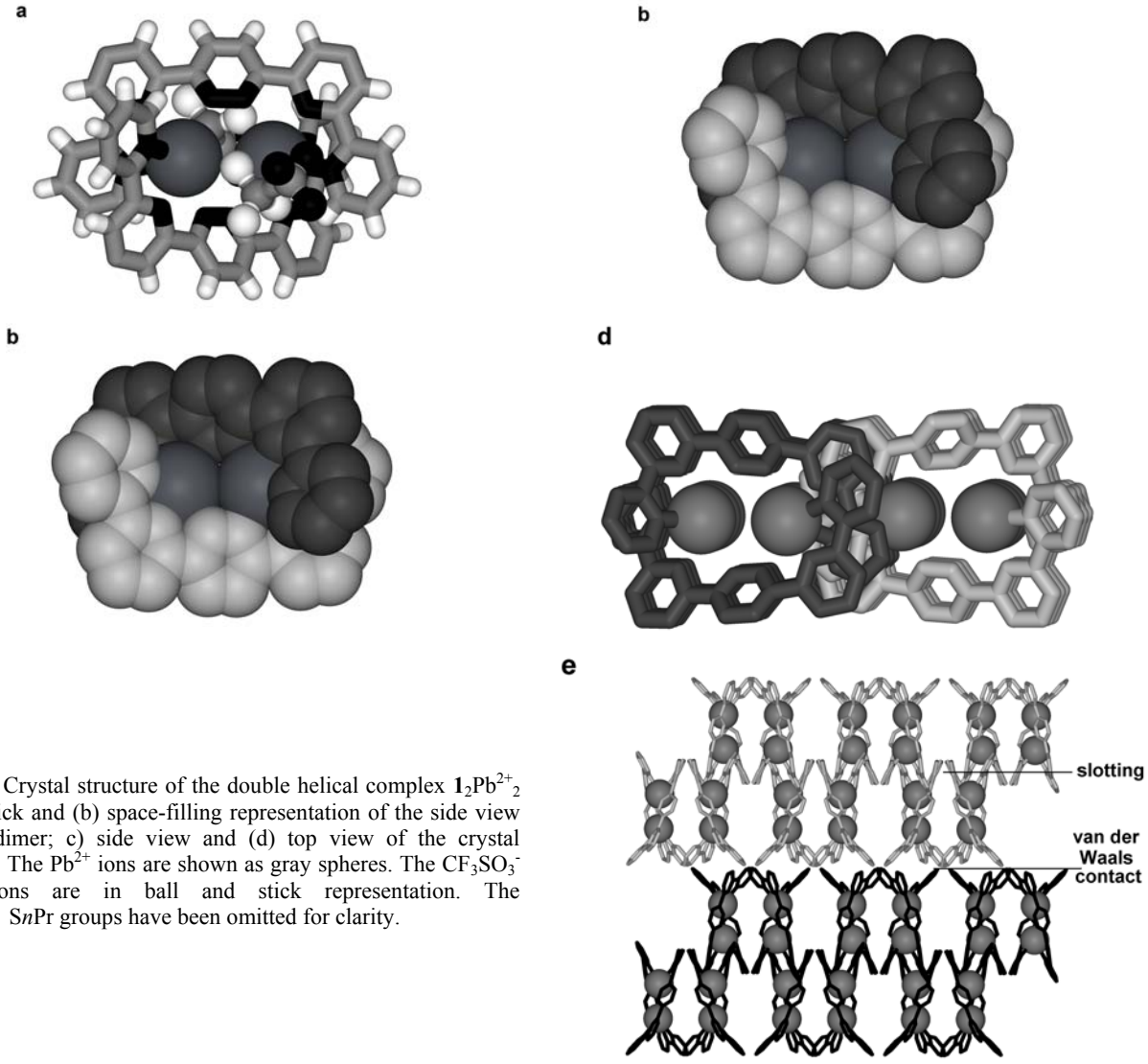


Fig. 3 – Crystal structure of the double helical complex $\mathbf{1}_2Pb^{2+}{}_2$ **7**: (a) stick and (b) space-filling representation of the side view of the dimer; c) side view and (d) top view of the crystal packing. The Pb^{2+} ions are shown as gray spheres. The $CF_3SO_3^-$ counterions are in ball and stick representation. The S*n*Pr groups have been omitted for clarity.

CONCLUSION

The above results describe the formation of coordination architectures derived from the ligand **1** and different metal ions (Co^{2+}, Cu^{2+}, Pb^{2+}). In terms of molecular adaptability the formation of rack-type and double helical architectures represent the best compromises between a rigid ligand, **1** with an unfavorable orientation of coordination vectors and the octahedral metal ions. The formation of the metalloarchitectures **5, 6** and **7** underlines the fact that, despite the role of the strength of the coordination interactions and of maximal site occupation, other factors like stacking, binding of anions (triflate, hydroxide or

tetrafluoroborate anions stabilizing the network of metallic ions) and of solvent molecules may interfere and influence the nature of the preferentially formed species.

Table 1

Coordination and intermetallic distances in complexes **5-7**.

Complex	D $_{Me}2+_{-NPy1}$ / Å	D $_{Me}2+_{-NPy2}$ / Å	D $_{Me}2+_{-NPy1}$ / Å	D $_{Me}2+_{-Me}2+$ / Å
5	2.15	2.04	2.25	3.94
6	1.96	1.90	1.98	3.19
7	2.47	2.61	2.70	3.89

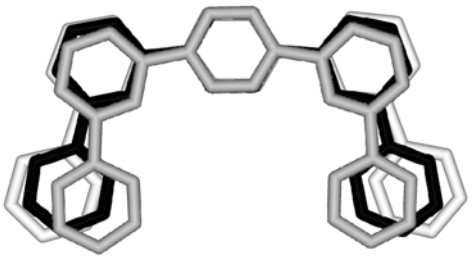


Fig. 4 – Change in the shape of the structure of the ligand **1** in metallosupramolecular architectures: Cu^{2+} complex **6** (gray), Co^{2+} complex **5** (black), Pb^{2+} complex **7** (white).

The coordination of metal ions of different coordination behaviors and the binding of different bridging anions lead to the change in the shape of **1**, from a compressed (**1**$Cu^{2+}{}_2$(OH), **6**) through a geometrically idealized (**1**$Co^{2+}{}_2$, **5**) to a distorted extended form ($1_2Pb^{2+}{}_2$, **7**) (Table 1, Figure 4). The close positioning of two metal ions with open coordination sites suggests potential use of ligand **1** and its metal complexes in dinuclear processes.

The structural features in solution and solid state make the species presented here (rack, squared-racks and double helix) of interest with respect to the general question of selection and adaptation of metallosupramolecular architectures as a function of ligand, metal ions and external entities.

EXPERIMENTAL PART

General methods. All reagents (acetylpyridine, **3**, $Co(BF_4)_2$, *t*BuOK, NH_4OAc) were obtained from commercial suppliers and used without further purification. THF was distilled over benzophenone/Na. All organic solutions were routinely dried by using sodium sulfate (Na_2SO_4). Column chromatography was carried out on Merck alumina activity II-III. $Pb(OTf)_2$ was prepared from PbO and CF_3SO_3H as previously reported.[4c] The microanalyses were carried out at Service de Microanalyses, Institut Charles Sadron, Strasbourg. ^{1}H NMR, ^{13}C NMR, COSY and ROESY were recorded on an ARX 300 MHz Bruker spectrometer in $CDCl_3$, with the use of the residual solvent peak as reference. Mass spectrometric studies were performed in the positive ion mode using a quadrupole mass spectrometer (Micromass, Platform 2+). Samples were dissolved in acetonitrile and were continuously introduced into the mass spectrometer at a flow rate of 10 mL/min through a Waters 616HPLC pump. The temperature (60°C), the extraction cone voltage (V_c=5-10V) was usually set to avoid fragmentations.

Synthesis of ligands and complexes

Experimental procedure for ligand 1: To a refluxing solution of **3** (0.43 g, 3.56 mmol) and *t*BuOK (0.8 g, 7.12 mmol) in dry THF (20 mL) a solution of **4**[7b] (1g, 1.78mmol) in dry THF (15 mL) was added under argon over a period of 2 h. The solution was stirred overnight at room temperature and acetic acid (1 mL) and NH_4OAc (1g) were added to the reaction. The mixture was refluxed for 90 min., cooled, poured into water (100 mL) extracted with chloroform (3x100 mL), washed with saturated aqueous $NaHCO_3$ (100 mL) and dried with Na_2SO_4. After evaporation the crude material was purified by flash chromatography (alumina/chloroform) to give **1** (0.68 g, 2 mmol 71.6%). ^{1}H NMR, ^{13}C NMR (300 MHz, $CDCl_3$), ESI-MS and elemental analysis were identical with those reported in reference 7b.

Complex 5: Formation from ligand **1** (10 mg, 18.6 mmol) and $Co(BF_4)_2$ $3H_20$ (6.3 mg, 18.6 mmol) in 0.5 mL CH_3CN at room temperature. ES-MS: m/z (%): 204.6 (100) [**1**$Co_2(CH_3CN)_4$]$^{4+}$.

Complex 6: Formation from ligand **1** (10 mg, 18.6 mmol) and $Cu(CF_3SO_3)_2$ (6.74 mg, 18.6 mmol) in 0.5 mL CH_3CN at room temperature. ES-MS: m/z (%): 281.9 (100) [**1**$Cu_2(CH_3CN)_4OH$]$^{3+}$.

Complex 7: Formation from ligand **1** (10 mg, 18.6 mmol) and and $Pb(CF_3SO_3)_2$ (9.3 mg, 18.6 mmol) in 0.5 mL CH_3CN at room temperature. ES-MS: m/z (%): 371.8 (100) [$\mathbf{1}_2Pb_2$]$^{4+}$.

X-Ray Crystallographic data for complexes 5, 6 and 7. X-ray diffraction data measurements for **5**-**7** were carried out at beamline ID11 at the European Synchrotron of Radiation Facility (ESRF) at Grenoble. A wavelength of 0.51593 Å was selected using a double crystal Si (111) monochromator and data were collected using a Bruker "Smart" CDD camera system at fixed 2θ. Crystals were placed in oil, mounted on a glass fibre and placed in a low-temperature N_2 stream. Data were reduced using the Bruker SAINT software. The structures determination and refinement were carried out with Shelxs[16] and Shelxl[17] respectively. All non-hydrogen atoms were refined anisotropically; hydrogen atoms were included at calculated positions by using a riding model.

Single crystals of **5**, [C_{43} $H_{48}B_4Co_2F_{16}N_{11}OS_2$] were grown from 1/5 acetonitrile/benzene solutions at room temperature. Measurement was carried out on a single pink crystal of dimension 0.16 x 0.12 x 0.06. The unit cell was triclinic with space group of P-1. Cell dimensions were a=10.0239(3, b=12.9366(4), c=23.1017(8, α=105.824(5), β=90.600(5), γ=104.288(5), V = 2783.3(2) $Å^3$ and Z=2. Of the 12287 reflections collected from 2.5 °≤ θ ≤ 27.56° 4670 were unique with 690 having I>2σ(I). The final number of parameters and constraints (on relative anisotropic displacement factors) were 534 and 146. Final R factors were R_1=0.0511 and wR_2=0.1301, (all observed data), (I>3σ(I)), minimum and maximal residual electron densities were –0.544 and 1.023 $eÅ^{-3}$.

Single crystals of **6**, [$C_{68}H_{32}F_{12}N_{12}O_{12}Cu_{12}$ S_{12}] were grown from 1/5 nitromethane /benzene solutions at room temperature. Measurement was carried out on a single green crystal of dimension of a single yellow crystal of dimensions 0.10 x 0.05 x 0.04. The unit cell was triclinic with space group of P-1. Cell dimensions were a=12.4289(5), b=12.8774(5), c=13.0794(4), α=92.559(1), β=94.955(1), γ=92.491 (2) V = 2081.13$Å^3$ and Z=4. Of the 12468 reflections collected from 8.92 °≤ θ ≤ 14.01° 6028 were unique with 5909 having I>4σ(I). Structure solution and refinement were carried out as for **4**. The final number of parameters was 626. Final R factors were R_1=0.0583 and wR_2=0.0763, (all observed data), (I>4σ(I)), minimum and maximal residual electron densities were –0.960 and 1.645 $eÅ^{-3}$.

Single crystals of **7**, [$C_{272}H_{128}N_{48}Pb_8F_{48}O_{48}S_{24}$] were grown from 1/5 acetonitrile/*i*-propylether solutions at room temperature. Measurement was carried out on a single red crystal of dimension 0.09 x 0.05 x 0.04 . The unit cell was triclinic with space group P2(1)/c. Cell dimensions were a=21.5080(3), b=14.2967(3), c=26.7890(3), α=90.000, β=102.448(1), γ=90.000, V = 8043.79$Å^3$ and Z=4. Of the 20852 reflections collected from 9.27 °≤ θ ≤ 14.97° 9832 were unique with 9245 having I>4σ(I). The final number of parameters was 1185. Final R factors were R_1=0.0454 and wR_2=0.1221, (all observed data), R_1=0.0219 and wR_2=0.0248(I>4σ(I)), minimum and maximal residual electron densities were –1.357 and 0.843 $eÅ^{-3}$.

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