*Dedicated to the memory of
 Professor Dumitru OANCEA (1941–2020)*

HETEROMETALLIC SUPRAMOLECULAR ARCHITECTURES CONSTRUCTED FROM CYANIDO-BASED $[\text{Co}^{\text{III}}(\text{AA})(\text{CN})_4]^-$ BUILDING-BLOCKS (AA = 1,10-PHENANTHROLINE AND 2,2'-BIPYRIDINE)

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A neutral, mixed-valence cyanido-bridged $\{\text{Co}_2^{\text{II}}\text{Co}_2^{\text{III}}\}$ complex, with formula $\{[\text{Co}^{\text{II}}_2(\text{L})(\text{MeOH})_2][\text{Co}^{\text{III}}(\text{phen})(\text{CN})_4]_2\} \cdot 2\text{H}_2\text{O} \cdot 0.5\text{MeOH}$ (**1**), and a cyanido-based ionic compound, with formula $[\text{Mn}^{\text{II}}(\text{MAC})(\text{H}_2\text{O})_2][\text{Co}^{\text{III}}(\text{bipy})(\text{CN})_4]_2 \cdot 3\text{H}_2\text{O}$ (**2**) were obtained by reacting the heteroleptic $\text{Ph}_4\text{P}[\text{Co}^{\text{III}}(\text{AA})(\text{CN})_4]^-$ building-block [AA = 1,10-phenanthroline, phen, (**1**) and 2,2'-bipyridine, bipy, (**2**)] with the dinuclear $\{\text{Co}_2^{\text{II}}\text{L}\}^{2+}$ (**1**) and mononuclear $\{\text{Mn}^{\text{II}}(\text{MAC})\}^{2+}$ (**2**) precursors, respectively [H_2L = macrocyclic Schiff-base obtained by condensation of 2,6-diformyl-*p*-cresol with 1,3-diaminopropane and MAC = 2,13-dimethyl-3,6,9,12,18-pentaazabicyclo-[12.3.1]octadeca-(18),2,12,14,16-pentaene]. The structures of **1** and **2** were determined by X-ray diffraction on single crystals. **1** is a neutral tetranuclear homometallic compound where two peripheral $[\text{Co}^{\text{III}}(\text{phen})(\text{CN})_4]^-$ entities which act as end-cap ligands through one of their four cyanide groups towards the inner double phenoxido-bridged $[\text{Co}_2^{\text{II}}(\text{L})(\text{MeOH})_2]^{2+}$ dinuclear unit. Both cobalt(III) and cobalt(II) ions are six-coordinate with two phenanthroline-nitrogen and four cyanide-carbon atoms (at Co^{III}) and two phenoxido-oxygens and two imino-nitrogen atoms from the Schiff-base ligand plus a methanol molecule and a cyanide-nitrogen atom (at Co^{II}) building somewhat distorted octahedral surroundings. The value of the cobalt(II)–cobalt(II) separation is 3.11 Å and that of the angle at the phenoxo bridge is 99.4°. Compound **2** is a heterobimetallic ionic salt which is made up of $[\text{Co}^{\text{III}}(\text{bipy})(\text{CN})_4]^-$ anions and $[\text{Mn}(\text{MAC})(\text{H}_2\text{O})_2]^{2+}$ cations. Each cobalt(II) in **1** is six-coordinated, in a distorted octahedral environment built by a bidentate bipy ligand and four monodentate cyanide groups whereas the manganese(II) ion is seven-coordinated with five nitrogen atoms of the MAC ligand and two water molecules describing a distorted pentagonal bipyramid surrounding. The cryomagnetic investigation of **1** in the temperature range 1.9–300 K reveals the occurrence of strong spin-orbit coupling effects and a relatively weak antiferromagnetic interaction between the high-spin cobalt(II) ions linked by the double phenoxido bridge. The nature and magnitude of the magnetic coupling in **1** compares well with those from previous magneto-structural studies on the $\text{Co}^{\text{II}}_2\text{O}_2$ motifs where antiferromagnetic interactions result in the examples having values at the phenoxido angle larger than 99.7° with dihedral angles smaller than 35.3°.

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INTRODUCTION

Cyanido complexes are efficient building-blocks for the construction of homo- and specially hereopolynuclear complexes, with different dimensionalities and topologies.¹ Homo- and heteroleptic paramagnetic cyanometallate such as $[M(CN)_6]^{3-}$, $[M(AA)(CN)_4]^-$, $[M'(CN)_8]^{3-}$ [$M = Cr^{III}$ and Fe^{III} ; $M' = Mo^V$ and W^V ; $AA = 2,2'$ -bipyridine (bipy), 1-10-phenantroline (phen), 2-(aminomethyl)pyridine (ampy) or 2,2'-bipyrimidine (bpym)] were extensively used to construct cyanido-bridged heterometallic compounds with interesting magnetic properties, due to the ability of cyanide ligand to mediate the magnetic coupling between the metal centers when acting as a bridge.¹⁻⁴ Conversely, the use of the diamagnetic cyanide-bearing building blocks have been much less explored.^{4a} Among them, $[Co^{III}(CN)_6]^{3-}$ and $[Mo^{IV}/W^{IV}(CN)_8]^{4-}$, were employed as metalloligands to build clusters or networks with remarkable magnetic properties. In this respect, among the great number of reported examples, we will cite herein only four of them: (i) a heptanuclear paramagnetic compound of formula $[\{ Cu^{II}(tren)(\mu-NC) \}_6 Mo^{IV}(CN)_2] (ClO_4)_8 \cdot 5H_2O$ [$tren = tris(2-aminoethyl)amine$] that undergoes a reversible intramolecular electron transfer upon light irradiation resulting in a high-spin molecule;⁵ (ii) a dodecanuclear $[\{ Cu^{II}(valen)Tb^{III} \}_4 \{ Mo^{IV}(CN)_8 \}_2]^{4+}$ complex cation [$H_2valen = N,N'$ -ethylenebis(3-methoxysalicylideneimine)] which behaves as a single-molecule magnet (SMM);⁶ (iii) the heterobimetallic dinuclear compound $[Mn^{III}(5-TMAM(R)-salmen)(H_2O)(\mu-NC)Co^{III}(CN)_5] \cdot 7H_2O \cdot MeCN$ [$5-TMAM(R)-salmen = (R)-N,N'$ -(1-methylethylene)bis(5-trimethylammoniomethyl-

salicylideneimine)] and (iv) the homometallic 2D network $[\{ Co^{II}(TODA) \}_3 \{ Co^{III}(CN)_6 \}_2] \cdot 9H_2O$ ($TODA = 1,4,10-trioxa-7,13-diazacyclopentadecane$) that show Single-Ion (SIM) and Single-Molecule Magnet (SMM) behaviors, respectively.^{7,8} To the best of our knowledge, only six examples of heterometallic complexes based on tetracyanidocobaltate(III) building-blocks were reported to date: two cyanido-bridged heterobimetallic chains of formulas $\{ [Mn^{III}(salen)(\mu-NC)_2Co^{III}(4,4'-dmbipy)(CN)_2] \cdot H_2O \}_n$ and $\{ [Mn^{III}(salen)(\mu-NC)_2Co^{III}(dmphen)(CN)_2] \cdot H_2O \}_n$ [$H_2salen = N,N'$ -ethylenebis(salicylideneimine), 4,4'-dmbipy = 4,4'-dimethyl-2,2'-bipyridine and dmphen = 2,9-dimethyl-1,10-phenanthroline],⁹ two trinuclear complexes, $[Co^{II}(phen)_2 \{ (\mu-NC)Co^{III}(phen)(CN)_3 \}_2] \cdot EtOH \cdot 2H_2O$ ^{10a} and $[Fe^{II}(phen)_2 \{ (\mu-NC)Co^{III}(phen)(CN)_3 \}_2] \cdot 4H_2O$,^{10b} and the two ionic salts, $[Co^{II}(phen)_3]_2[Co^{III}(CN)_6][Co^{III}(phen)(CN)_4] \cdot 8H_2O$ and $[Co^{II}(bipy)_3][Co^{III}(bipy)(CN)_4]_2 \cdot H_2O$.¹¹

In this work, we show how the use of the heteroleptic compound $PPh_4[Co^{III}(AA)(CN)_4]$ ($AA = bipy$ or $phen$) as a metalloligand towards the preformed species $\{Co_2^{II}L\}^{2+}$ and $\{Mn(MAC)\}^{2+}$ [see Scheme 1; $H_2L =$ macrocyclic Schiff-base obtained by condensation of 2,6-diformyl-*p*-cresol with 1,3-diaminopropane and $MAC =$ macrocyclic Schiff-base resulting from the condensation reaction of 2,6-diacetylpyridine and triethylenetetramine] affords the cyanido-based complexes of formulas $[Co^{II}(L)(MeOH)_2(\mu-CN)_2 \{ Co^{III}(phen)(CN)_2 \}_2] \cdot 2H_2O \cdot 0.5MeOH$ (**1**) and $[Mn^{II}(MAC)(H_2O)_2] [Co^{III}(bipy)(CN)_4]_2 \cdot 3H_2O$ (**2**). The preparation and structural characterization of **1** and **2** together with the cryomagnetic study of **1** are presented herein.

Scheme 1

RESULTS AND DISCUSSION

Synthesis and infrared spectroscopy

The preparation of **1** and **2** is carried out in a straightforward way, in a single step process, by using the stable $[\text{Co}^{\text{III}}(\text{AA})(\text{CN})_4]^-$ complex anion as a metalloligand against the preformed species $\{\text{Co}_2^{\text{II}}\text{L}\}^{2+}$ (**1**) and $\{\text{Mn}(\text{MAC})\}^{2+}$ (**2**). The electroneutrality in **1** is achieved by the monodentate coordination of a $[\text{Co}^{\text{III}}(\text{phen})(\text{CN})_4]^-$ unit to each cobalt(II) ion of $\{\text{Co}_2^{\text{II}}\text{L}\}^{2+}$, and it is most likely at the origin of its precipitation from the solution. Compound **2** instead, seems to be a kinetic product because one might expect the formation of neutral trinuclear complex if the two coordinated solvent molecules in axial positions at the manganese(II) ion were replaced by peripheral cyanides of the $[\text{Co}^{\text{III}}(\text{bipy})(\text{CN})_4]^-$ unit. The FTIR spectrum of **1** displays medium intensity bands at 2159 and 2130 cm^{-1} characteristic for the stretching vibrations of the bridging and terminal cyanido groups, values higher than the peak at 2126 cm^{-1} which is specific to the terminal cyanido ligands of the cyanometallate precursor, $[\text{Co}^{\text{III}}(\text{phen})(\text{CN})_4]^-$. The intense band at 1635 cm^{-1} is assigned to the imino group from the macrocyclic Schiff-base ligand, L^{2-} , which accommodates the two Co^{II} ions. The FTIR spectrum of the $\text{PPh}_4[\text{Co}^{\text{III}}(\text{bipy})(\text{CN})_4]^-$ complex shows a medium intense band at 2126 cm^{-1} which is assigned to the terminal cyanido groups. This band is split and shifted to higher wavenumbers (at ca. 2132 and 2141 cm^{-1}) in the FTIR spectrum of the $[\text{Co}^{\text{III}}(\text{bipy})(\text{CN})_4]^-$ in **2** because of the non-equivalence of their cyanide ligands, three of the four ones being involved, as hydrogen bond acceptors, in hydrogen bonds with free and coordinated water molecules (*vide infra*). The peaks at 3281 and 1651 cm^{-1} in the infrared spectra of **2** correspond to N-H and imine $\text{C}=\text{N}$ stretching vibrations of the MAC ligand. Finally, the ring-stretching modes of the phen and bipy ligands overlap in the 1630–1560 cm^{-1} region.

Description of the structure of compound 1

The crystal structure of **1** consists of tetranuclear mixed valence $\{\text{Co}_2^{\text{III}}\text{Co}_2^{\text{II}}\}$ motifs where two peripheral $[\text{Co}^{\text{III}}(\text{phen})(\text{CN})_4]^-$ entities act as monodentate ligands towards an inner $\{\text{Co}_2^{\text{II}}\text{L}(\text{MeOH})_2\}^{2+}$ dinuclear unit (see Fig. 1).

Water and methanol molecules of crystallization are also present.

Within the mononuclear cobalt(III) anionic moiety, $[\text{Co}^{\text{III}}(\text{phen})(\text{CN})_4]^-$, the cobalt ion is surrounded by two nitrogen atoms, from a bidentate phen molecule, and by four cyanide carbon atoms, leading to a somewhat distorted octahedral environment. The short bite of the chelating phen [$\text{N}5\text{--Co}1\text{--N}6 = 83.12(12)^\circ$] is the main source of this distortion. The $\text{Co}1\text{--C}_{\text{cyanide}}$ and $\text{Co}1\text{--N}_{\text{phen}}$ bond distances cover the ranges 1.862(4)–1.904(4) and 1.965(3)–1.981(3) Å, respectively and their values are as expected.^{9–12} The bis-monodentate cyanide group and the phen ligand are in-plane. All the cyanide ligands are quite linearly coordinated to the metal ion, with $\text{Co}\text{--C}\text{--N}$ angles spanning the range 176.1(3)–178.3(4) $^\circ$. Regarding the dinuclear $\{\text{Co}_2^{\text{II}}\text{L}\}^{2+}$ cationic fragment, the compartmental Schiff-base ligand encompasses the two metal ions, which are connected by the phenoxido groups. Each cobalt(II) ion adopts a distorted octahedral coordination geometry with two imine-nitrogen and two μ -phenoxido-oxygen atoms in the equatorial positions [2.052(2)/2.021(2) Å for $\text{Co}2\text{--O}1/\text{O}1a$ and 2.046(3)/2.044(3) Å for $\text{Co}2\text{--N}7/\text{N}8$; symmetry code: (a) = 2-x, -y, 2-z] and an oxygen atom from a methanol molecule and one nitrogen atom from a cyanido-bridge [$\text{Co}2\text{--O}1M$ and $\text{Co}2\text{--N}3$ bond distances of 2.287(3) and 2.153(3) Å, respectively] occupying the axial positions. The two cobalt(II) metal ions and the two μ -phenoxido-oxygen atoms are coplanar, for symmetry reasons, with a dihedral angle of 0.00(8) $^\circ$; the phenoxido-oxygen bridges separate the two $\text{Co}(\text{II})$ ions by 3.108(1) Å, the $\text{Co}\text{--O}\text{--Co}$ angle being 99.43(10) $^\circ$. The coordination fashion of the bis-monodentate cyanide group toward the $\text{Co}(\text{II})$ ion of the central cationic moiety is significantly bent, the $\text{Co}2\text{--N}3\text{--C}3$ angle measuring 156.9(3) $^\circ$; the $\text{Co}1\cdots\text{Co}2$ distance across such cyanide bridge is 5.04 Å.

The $\{\text{Co}_2^{\text{II}}\text{Co}_2^{\text{III}}\}$ tetramers are inter-connected through $\text{O}\cdots\text{N}$ hydrogen-bonds involving two of the three monodentate cyanide ligands of the outer $[\text{Co}^{\text{III}}(\text{phen})(\text{CN})_4]^-$ fragments, the methanol molecules coordinated to the $\text{Co}(\text{II})$ ions in the central $[\text{Co}_2^{\text{II}}\text{L}(\text{MeOH})_2]^{2+}$ binuclear unit, and the water molecules of crystallization (see Fig. 2, left and Table 1). These interactions, overall, result in a three-dimensional supramolecular network (see Fig. 2, right).

Fig. 1 – A view of the structure of the tetranuclear unit in **1** together with selected atomic labels. Hydrogen atoms, water and disordered methanol molecules of crystallization were omitted for clarity [Symmetry code: (a) = $2-x, -y, 2-z$].

Fig. 2 – Details of the crystal packing of **1**: (left) a view of one $\{\text{Co}_2^{\text{II}}\text{Co}_2^{\text{III}}\}$ tetranuclear unit in its immediate environment, highlighting the H-bonding interactions; (right) a view of the 3-D hydrogen-bond supramolecular network in the crystallographic *bc* plane of **1**. The macrocyclic Schiff base, the phen ligand and one cyanide ligand were omitted for the sake of clarity. Symmetry codes: $a = x, y, 1+z$; $b = \frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$; $c = 1+x, y, z$.

Table 1

Selected intermolecular contacts (Å) for **1***

D-H...A	D-H (Å)	H...A (Å)	D...A (Å)	Angle D-H...A
O1W ^a -H1W ^a ...N1	0.97(3)	2.08(3)	3.019(5)	163(5)
O1W ^b -H2W ^b ...N4	0.98(4)	1.92(3)	2.854(5)	159(4)
O1M...N1 ^{c#}			2.891	

*Symmetry codes: (a) = $x, y, 1+z$; (b) = $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$; (c) = $1+x, y, z$. # The hydrogen atom from the OH group of the coordinated methanol molecule could not be found.

Description of the structure of compound **2**

Compound **2** crystallizes in the acentric triclinic space group *P*1. The asymmetric unit is made of one $[\text{Mn}^{\text{II}}(\text{MAC})(\text{H}_2\text{O})_2]^{2+}$ complex cation, two crystallographically independent $[\text{Co}^{\text{III}}(\text{bipy})(\text{CN})_4]$ complex anions, and three crystallization water molecules (see Fig. 3).

Within the mononuclear Co^{III} molecular anions, both Co1 and Co2 atoms are six-coordinate by four cyanide-carbon atoms and two bipy-nitrogen

atoms, in a distorted octahedral geometry. The values of the angles subtended by the chelating bipy molecules at the cobalt atoms are 82.1(3) and 82.0(3)° for N1-Co1-N2 and N7-Co2-N8, respectively. Bond distances and angles are very similar for the two complexes. The bipy bite angle is 82.1(3)° at Co1 and 82.0(3)° at Co2. The Co-C and Co-N bond distances are consistent with those observed in **1** as well as with literature values.^{11,13} The former cover the ranges 1.867(7)-1.921(9) for Co1 and 1.882(8)-1.929(8) for Co2, while the latter

values are 1.975(6)-1.979(6) at Co1 and 1.979(6)-1.991(6) Å at Co2. Likewise to **1**, all the cyanide ligands are rather linearly coordinated to the metal ion, with Co-C-N angles spanning the ranges 177.2(6)-177.9(8)° for Co1 and 175.2(8)-178.2(8)° for Co2. Within the molecular cation, the manganese atom is seven-coordinate by five nitrogen atoms from the pentadentate macrocyclic ligand in the equatorial positions and two *trans* positioned water molecules occupying the axial sites of a distorted pentagonal bipyramid environment. The Mn1-N [values in the range 2.244(7)-2.373(8) Å] and Mn1-O_w [2.258(6) and

2.329(5) Å] bond distances agree with those reported for this complex cation in the [Mn^{II}(MAC)(H₂O)₂]Cl₂·4H₂O¹⁴ and [Mn^{II}(MAC)(μ-NC)₂Co^{III}(μ-2,5-dpp)(CN)₆]_n·7nH₂O complexes [2,5-dpp = 2,5-bis(2-pyridyl)pyrazine].¹⁵

A 3-D supramolecular network arising from a variety of hydrogen bonds and, to a lesser extent, π···π stacking interactions, can be noted in the crystal packing of **2** (Figs. 4–6). A detailed picture of the hydrogen bonds is depicted in Fig. 4, and the data corresponding to the hydrogen bonds are gathered in Table 2.

Fig. 3 – Perspective view of the asymmetric unit of **2**, along with selected atomic labels. The hydrogen atoms and the free water molecules were omitted for clarity.

Fig. 4 – Comprehensive view of the O···N and O···O type hydrogen-bonds in **2**. Phen and MAC ligands and a few cyanide groups are not shown for the sake of clarity. Symmetry codes: *a* = -1+*x*, 1+*y*, *z*; *b* = *x*, *y*, -1+*z*; *c* = -1+*x*, *y*, *z*; *d* = *x*, 1+*y*, -1+*z*; *e* = -1+*x*, 1+*y*, -1+*z*; *f* = *x*, -1+*y*, *z*; *g* = *x*, 1+*y*, *z*.

Table 2
Hydrogen bonding interactions (Å and °) for **2***[&]

D-H...A	D-H (Å)	H...A (Å)	D...A (Å)	Angle D-H...A
O1W-H1W...O3W	0.94(6)	1.93(7)	2.846(10)	164(7)
O1W-H2W...O5W	0.94(6)	1.91(6)	2.704(7)	141(8)
O2W-H3W...N11 ^a	0.92(6)	2.02(7)	2.893(9)	158(7)
O2W-H4W...O4W	0.93(5)	1.76(5)	2.688(8)	171(8)
O3W-H5W...O2W ^b	0.95(10)	2.14(9)	3.072(9)	165(8)
O3W-H6W...N4 ^b	0.95(8)	2.09(10)	2.869(10)	138(8)
O4W-H7W...N10	0.91(7)	2.01(7)	2.887(10)	161(8)
O4W-H8W...N9 ^c	0.93(7)	1.97(8)	2.879(11)	166(6)
O5W-H9W...N6 ^d	0.94(7)	2.06(7)	2.867(10)	143(6)
O5W-H10W...N5 ^e	0.93(6)	2.08(7)	2.891(10)	145(7)

*D = donor and A = acceptor. [&]Symmetry codes: (a) = -1+x, 1+y, z; (b) = x, y, -1+z; (c) = -1+x, y, z; (d) = x, 1+y, -1+z; (e) = -1+x, 1+y, -1+z.

Fig. 5 – A portion of the crystal packing showing the multitude of O...O and O...N hydrogen-bonds (light-green dashed lines) giving rise to supramolecular walls (stacked ribbons) in **2**.

Each $[\text{Mn}(\text{MAC})(\text{H}_2\text{O})_2]^{2+}$ cation is connected to two crystallographically independent $[\text{Co}(\text{phen})(\text{CN})_4]^-$ anions through one crystallization water-mediated O...O...N [O1W...O3W...N4^b, the Mn1...Co1^b separation being 7.888(1) Å] and one direct O...N [O2W...N11^a, $a = -1+x, 1+y, z$, the Mn1...Co2^a separation being 6.766(1) Å] H-bonds. The resulting supramolecular trinuclear assemblies line up along the crystallographic [100] direction and give rise to a supramolecular ribbon in the crystallographic *ac* plane through further H-bonding interactions mediated by the crystallization water molecules [O1W...O3W...O2W^b, O1W...O5W...N5^e, O2W...O4W...N10, $b = x, y, -1+z$; $e = -1+x, 1+y, -1+z$] (see Figs. 4 and 5). In turn, the ribbons are stacked along the crystallographic *b* axis and

interconnected along this direction as well by two indirect O...O...N hydrogen bonds [O1W...O5W...N6^d and O2W...O4W...N9^c, $c = -1+x, y, z$; $d = x, 1+y, -1+z$], thus forming supramolecular “walls” of anionic and cationic units in **2**. Within the described H-bonding network, all crystallization water molecules (O3W, O4W and O5W) act as supramolecular “bridges” by extensively connecting the ionic entities (see also Table 2).

Lastly, weak $\pi\cdots\pi$ stacking interactions partially involving the bipy ligands of the $[\text{Co}(\text{bipy})(\text{CN})_4]^-$ molecular anions can be noted in **2** along the crystallographic *c* axis [with centroid...centroid distance of 3.91 Å and interplanar distance of ca. 3.5 Å], interdigitating adjacent supramolecular “walls” in the same direction (Fig. 6).

Fig. 6 – A view of a fragment of the supramolecular 3D network of H-bonds and stacking interactions in **2**. Hydrogen bonds are drawn as light-green dashed lines and $\pi \cdots \pi$ stacking interactions are highlighted in the inset.

Magnetic properties of **1**

The magnetic properties of **1** in the form of $\chi_M T$ versus T plot [χ_M is the magnetic susceptibility per $\{\text{Co}^{\text{II}}_2\text{Co}_2^{\text{III}}\}$ tetranuclear unit) are shown in Fig. 7. At room temperature, the value of $\chi_M T$ product is $5.30 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$, a value which is greater than the spin-only value for two high-spin Co^{II} ions ($\chi_M T = 3.75 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ for $S_{\text{Co}} = 3/2$ and $g_{\text{Co}} = 2.0$) because of the contribution of the orbital angular momentum to

the electronic ground term $^4T_{2g}$ of octahedral environment around cobalt(II) ions. Upon cooling, the values of $\chi_M T$ continuously decrease and tend to vanish reaching $0.09 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$, at 5.0 K. The presence of a maximum in the susceptibility plot at 20.0 K is indicative of the occurrence of a relatively important antiferromagnetic interaction between the two cobalt(II) ions through the double phenoxido bridge.

Fig. 7 – Temperature dependence of the $\chi_M T$ product (o) and χ_M (Δ) for **1**. The solid lines are the best-fit curve through eq (1) (see text).

Because of the important first-order orbital momentum exhibited by the six-coordinated high-spin cobalt(II) ion, the Hamiltonian to treat its magnetic data has to be supplemented by the

$$H = -JS_{\text{Co1}} \cdot S_{\text{Co2}} - \sum_i \alpha_i \lambda_i L_i S_i + \sum_i \Delta_i [L_{z,i} - 2/3] + \beta H \sum_i (-\alpha_i L_i + g_e S_i) \quad (1)$$

where i runs over the two cobalt(II) ions. The first term in this Hamiltonian accounts for the magnetic coupling between the two spin quartets ($S_{\text{Co2}} = S_{\text{Co2a}} = 3/2$), the second one stands for the spin-orbit coupling of the 4T_1 ground term, the third one deals with the splitting of the T_1 orbital term in a singlet and a doublet orbital term (Δ being the energy gap) due to an axial symmetry, and the fourth one is the Zeeman interaction. Due to the centrosymmetry of the diphenoxido-bridged dicobalt(II) unit of **1**, $\alpha_1 = \alpha_2 = \alpha$, $\lambda_1 = \lambda_2 = \lambda$ and $\Delta_1 = \Delta_2 = \Delta$. Least-squares fit of the magnetic susceptibility data of **1** gave $J = -7.12 \text{ cm}^{-1}$, $\lambda = -150 \text{ cm}^{-1}$, $\alpha = 1.19$, $\Delta = 500 \text{ cm}^{-1}$ with $R = 2.8 \times 10^{-5}$ (R is the agreement factor defined as $\sum_i [(\chi_M)_{\text{obs}}(i) - (\chi_M)_{\text{calc}}(i)]^2 / \sum_i [(\chi_M)_{\text{obs}}(i)]^2$). The calculated χ_M and $\chi_M T$ curves (solid lines in Fig. 7) match well the magnetic data in the whole temperature range explored.

Alternatively, given the relatively important antiferromagnetic coupling observed in **1**, the analysis of its magnetic data of **1** were also treated through the Hamiltonian of eq (2)

$$H = -JS_{\text{Co1}} \cdot S_{\text{Co2}} + \beta H \sum_i g_e S_i \quad (2)$$

A somewhat lower quality fit was achieved, the best-fit parameters being as follows: $J = -7.85 \text{ cm}^{-1}$, $g = 2.42$ and $TIP = 1020 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ with $R = 1.8 \times 10^{-4}$. TIP is the temperature independent paramagnetism and its large value has to be attributed to the spin-orbit coupling effects.

The values of the α , λ and Δ parameters for **1** are in the range of those observed in other magneto-structurally investigated six-coordinated high-spin cobalt(II) complexes.¹⁷⁻²¹ As far as the value of the magnetic interaction is concerned, the two approaches provide close values of the magnetic coupling between the two cobalt(II) ions through the double phenoxido bridge. Both its nature and magnitude are as expected in the light of the previous studies on similar diphenoxido-bridged dicobalt(II) systems.²²⁻²⁶ In fact, these studies have shown that the angle at the phenoxido bridge (γ) and the the dihedral angle between the Co-O-Co plane and the phenyl plane (δ) are determinant in order to cause an antiferro- or ferromagnetic coupling between the two high-spin

inclusion orbitally dependent exchange as well as spin-orbit coupling effects. Consequently, the magnetic properties of **1** were analyzed through the Hamiltonian of eq (1)¹⁶

cobalt(II) ions, although there is no clear correlation between these two structural parameters for the Co_2O_2 motif.²⁶ The smaller γ and the larger δ values favor the ferromagnetic interaction in this family of dicobalt(II) complexes. In the case of **1**, γ and δ are equal to 99.4 and 16.9° respectively, values that lie in the antiferromagnetic domain.

EXPERIMENTAL

Materials. All reagents and solvents were purchased from commercial sources and used without further purification. The $[\text{Mn}^{\text{II}}(\text{MAC})(\text{H}_2\text{O})_2]\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ and $[\text{Co}^{\text{II}}_2\text{L}](\text{NO}_3)_2$ precursors were synthesized according to the previously described methods.^{14,23}

Synthesis of $[\text{Co}^{\text{II}}(\text{L})(\text{MeOH})_2(\mu\text{-CN})_2\{\text{Co}^{\text{III}}(\text{phen})(\text{CN})_2\}_2] \cdot 2\text{H}_2\text{O} \cdot 0.5\text{MeOH}$ (1**):** an acetonitrile-methanol solution (20 mL, 1:1 v/v) of 1 mmol (0.05 g) of $[\text{Co}^{\text{II}}_2\text{L}](\text{NO}_3)_2$ was layered, in a test tube, over an acetonitrile solution (20 mL) of 1 mmol (0.056 g) of $\text{PPh}_4[\text{Co}(\text{phen})(\text{CN})_4]$ affording X-ray quality crystals of **1** after two weeks. Yield: ca. 60 %. IR (KBr/ cm^{-1}): 3382(s), 3281(s), 2141(s), 2132(s), 1651(m), 1605(m), 1448(m), 777(vs). Anal. calcd. for $\text{C}_{117}\text{H}_{112}\text{Co}_8\text{N}_{32}\text{O}_{13}$ (**1**): C 53.11; H 4.16; N 17.15. Found: C 53.79; H 3.98; N 17.11 %.

Synthesis of $[\text{Mn}^{\text{II}}(\text{MAC})(\text{H}_2\text{O})_2][\text{Co}^{\text{III}}(\text{bipy})(\text{CN})_4]_2 \cdot 3\text{H}_2\text{O}$ (2**):** a methanol/acetonitrile solution (20 mL, 1:1 v/v) of 1/2 mmol (0.026 g) of $[\text{Mn}^{\text{II}}(\text{MAC})(\text{H}_2\text{O})_2]\text{Cl}_2$ was layered, in a test tube, over a methanol/acetonitrile solution (20 mL, 1:1 v/v) of 1 mmol (0.034 g) of $\text{PPh}_4[\text{Co}(\text{bipy})(\text{CN})_4]$ giving rise to X-ray quality crystals of **2**, after four weeks. Yield: ca. 50 %. IR (KBr/ cm^{-1}): 3382(s), 3281(s), 2141(s), 2132(s), 1651(m), 1605(m), 1448(m), 777(vs). Anal. calcd. for $\text{C}_{43}\text{H}_{49}\text{Co}_2\text{N}_{17}\text{O}_5\text{Mn}$: C 48.86; H 4.67; N 22.53. Found: C 48.81; H 4.61; N 22.50 %.

Physical measurements. FTIR spectra (4000-300 cm^{-1}) were recorded on a Bruker FS55 spectrophotometer on samples of **1** and **2** prepared as KBr pellets. Variable-temperature (1.9-300 K) magnetic susceptibility measurements on a polycrystalline sample of **1** were carried out with a SQUID susceptometer using applied magnetic fields of 1 T ($T \leq 50$ K) and 500 G ($T < 50$ K). Diamagnetic corrections for the constituent atoms were made by using the Pascal's constants. The magnetic data were also corrected for the magnetization of the sample holder (a plastic bag).

X-ray data collection and structure refinement. Diffraction data on single crystals of **1** and **2** were collected at room

temperature with a Bruker-Nonius X8-APEXII CCD area detector system by using graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å). The data were processed through the *SAINTE*¹⁷ reduction and *SADABS*¹⁸ absorption software. A summary of the crystallographic data and structure refinement for the two compounds is given in Table 3; main bond lengths and angles are shown in Tables 4-5. The structures were solved by direct methods and subsequently completed by Fourier recycling using the *SHELX*-2013 software package,¹⁹ then refined by the full-matrix least-squares refinements based on F^2 with all observed reflections. All non-hydrogen atoms of **1** and **2** were refined anisotropically. All the hydrogen atoms of the phen (**1**), bipy (**2**), the Schiff-base (**1**) and the MAC ligand (**2**) were set in calculated positions and refined isotropically using the riding model. The hydrogen atoms of either the coordinated or uncoordinated water molecules in both **1** and **2** were located from the Fourier difference map and refined with restraints on O–H and H $\cdots$ H distances. The H atoms of the coordinated methanol molecule in **1**, excluding the hydroxyl-H atom (not

found neither calculated), were refined isotropically in calculated positions; the uncoordinated methanol molecule in **1** was found pretty disordered and it was assigned an estimated occupancy of 0.25. No H atoms were thus located for this molecule. Regarding compound **2**, the possibility to solve the structure in the centrosymmetric space group *P*1 was carefully evaluated. Such investigation showed that it is indeed possible to solve the structure in *P*1, but the solution is quite inelegant, and the refining is much worse. The whole $[\text{Mn}(\text{MAC})(\text{H}_2\text{O})_2]^{2+}$ complex in *P*1 appears disordered over the inversion center. The R_1 and wR_2 values in *P*1 are about 0.12 and 0.30. Thus, we believe that solving the structure in *P*1 is the best option for this species.

Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre and have been assigned CCDC reference numbers 2045465 (**1**) and 2045466 (**2**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 3

Crystal data and details of structure determination for **1** and **2**.

	1	2
Formula	C _{58.50} H ₅₆ Co ₄ N ₁₆ O _{6.50}	C ₄₃ H ₄₉ Co ₂ MnN ₁₇ O ₅
Fw	1322.91	1056.79
<i>T</i> (K)	296(2)	296(2)
Crystal system	Monoclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 1
<i>a</i> /Å	10.4196(3)	8.5069(5)
<i>b</i> /Å	16.2615(5)	8.9461(5)
<i>c</i> /Å	17.4096(5)	17.3896(10)
α /deg	90.00	83.057(2)
β /deg	90.298(2)	79.250(3)
γ /deg	90.00	73.853(3)
<i>V</i> /Å ³	2949.81(15)	1245.55(13)
<i>Z</i>	2	1
<i>D</i> _c /g cm ⁻³	1.489	1.409
μ /mm ⁻¹	1.171	0.968
<i>F</i> (000)	1358	545
Refl. Collected	147139	29054
Refl. indep. [<i>R</i> _{int}]	6427 [0.1139]	9455 [0.0321]
Refl. obs. [<i>I</i> > 2 σ (<i>I</i>)]	4133	7770
Data/restraints/param.	6427/11/402	9455/18/646
Goodness-of-fit on F^2	1.037	1.018
^a Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0447 <i>wR</i> ₂ = 0.1025	<i>R</i> ₁ = 0.0440 <i>wR</i> ₂ = 0.1034
^b <i>R</i> indices (all data)	<i>R</i> ₁ = 0.0933 <i>wR</i> ₂ = 0.1240	<i>R</i> ₁ = 0.0588 <i>wR</i> ₂ = 0.1116
$\Delta\rho_{\text{max, min}}$ /e Å ⁻³	0.601 / -0.366	0.757 / -0.359
Abs. struct. param.	<i>n/a</i>	0.33(2)

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; ^b $wR_2 = \{\sum w(F_o^2 - F_c^2)^2 / \sum [w(F_o^2)^2]\}^{1/2}$ and $w = 1/[\sigma^2(F_o)^2 + (mP)^2 + nP]$ with $P = (F_o^2 + 2F_c^2)/3$, $m = 0.0598$ (**1**) and 0.0623 (**2**), and $n = 0.0623$ (**1**) and 0.2611 (**2**).

Table 4

Selected bond lengths (Å) and angles (deg) for **1***

Co(1)-C(3)	1.862(4)	Co(2)-O(1a)	2.021(2)
Co(1)-C(2)	1.866(4)	Co(2)-N(8)	2.044(3)
Co(1)-C(4)	1.901(4)	Co(2)-N(7)	2.046(3)
Co(1)-C(1)	1.904(4)	Co(2)-O(1)	2.052(2)
Co(1)-N(5)	1.965(3)	Co(2)-N(3)	2.153(3)
Co(1)-N(6)	1.981(3)	Co(2)-O(1M)	2.287(3)
C(3)-Co(1)-C(2)	90.23(16)	O(1a)-Co(2)-N(8)	91.19(11)
C(3)-Co(1)-C(4)	88.09(16)	O(1a)-Co(2)-N(7)	169.69(11)
C(2)-Co(1)-C(4)	88.63(18)	N(8)-Co(2)-N(7)	98.31(12)
C(3)-Co(1)-C(1)	90.08(16)	O(1a)-Co(2)-O(1)	80.57(10)
C(2)-Co(1)-C(1)	91.65(18)	N(8)-Co(2)-O(1)	168.60(11)
C(4)-Co(1)-C(1)	178.15(16)	N(7)-Co(2)-O(1)	89.47(11)
C(3)-Co(1)-N(5)	93.74(14)	O(1a)-Co(2)-N(3)	96.83(11)
C(2)-Co(1)-N(5)	175.61(15)	N(8)-Co(2)-N(3)	95.34(12)
C(4)-Co(1)-N(5)	89.65(15)	N(7)-Co(2)-N(3)	86.33(12)
C(1)-Co(1)-N(5)	90.20(15)	O(1)-Co(2)-N(3)	93.46(11)
C(3)-Co(1)-N(6)	176.44(14)	O(1a)-Co(2)-O(1M)	88.93(10)
C(2)-Co(1)-N(6)	92.85(14)	N(8)-Co(2)-O(1M)	83.41(11)
C(4)-Co(1)-N(6)	90.20(14)	N(7)-Co(2)-O(1M)	88.18(11)
C(1)-Co(1)-N(6)	91.61(14)	O(1)-Co(2)-O(1M)	88.54(9)
N(5)-Co(1)-N(6)	83.12(12)	N(3)-Co(2)-O(1M)	174.14(11)

*Symmetry code: $a = x, y, 1+z$.

Table 5

Selected bond lengths (Å) and angles (deg) for **2**

Co(1)-C(11)	1.913(8)	Co(2)-C(25)	1.924(8)	Mn(1)-N(13)	2.244(7)
Co(1)-C(12)	1.867(7)	Co(2)-C(26)	1.882(8)	Mn(1)-N(14)	2.264(8)
Co(1)-C(13)	1.894(8)	Co(2)-C(27)	1.905(8)	Mn(1)-N(15)	2.373(8)
Co(1)-C(14)	1.921(9)	Co(2)-C(28)	1.929(8)	Mn(1)-N(16)	2.334(7)
Co(1)-N(1)	1.975(6)	Co(2)-N(7)	1.979(6)	Mn(1)-N(17)	2.369(8)
Co(1)-N(2)	1.979(6)	Co(2)-N(8)	1.991(6)	Mn(1)-O(1W)	2.258(6)
				Mn(1)-O(2W)	2.329(5)
C(12)-Co(1)-C(13)	87.3(3)	C(26)-Co(2)-C(28)	89.7(3)	N(13)-Mn(1)-N(16)	145.8(2)
C(12)-Co(1)-C(11)	90.7(3)	C(27)-Co(2)-C(28)	91.0(3)	O(1W)-Mn(1)-N(16)	94.1(2)
C(13)-Co(1)-C(11)	89.4(3)	C(25)-Co(2)-C(28)	177.8(4)	N(14)-Mn(1)-N(16)	74.0(3)
C(12)-Co(1)-C(14)	88.5(3)	C(26)-Co(2)-N(7)	94.2(3)	O(2W)-Mn(1)-N(16)	86.4(2)
C(13)-Co(1)-C(14)	89.4(3)	C(27)-Co(2)-N(7)	176.6(3)	N(13)-Mn(1)-N(17)	140.4(3)
C(11)-Co(1)-C(14)	178.6(3)	C(25)-Co(2)-N(7)	90.6(3)	O(1W)-Mn(1)-N(17)	82.7(2)
C(12)-Co(1)-N(1)	96.0(3)	C(28)-Co(2)-N(7)	90.4(3)	N(14)-Mn(1)-N(17)	146.5(3)
C(13)-Co(1)-N(1)	176.3(3)	C(26)-Co(2)-N(8)	176.0(3)	O(2W)-Mn(1)-N(17)	99.1(2)
C(11)-Co(1)-N(1)	89.0(3)	C(27)-Co(2)-N(8)	94.9(3)	N(16)-Mn(1)-N(17)	73.7(3)
C(14)-Co(1)-N(1)	92.2(3)	C(25)-Co(2)-N(8)	93.3(3)	N(13)-Mn(1)-N(15)	69.3(2)
C(12)-Co(1)-N(2)	177.4(3)	C(28)-Co(2)-N(8)	88.8(3)	O(1W)-Mn(1)-N(15)	90.8(2)

Table 5 (continued)

C(13)-Co(1)-N(2)	94.6(3)	N(7)-Co(2)-N(8)	82.0(3)	N(14)-Mn(1)-N(15)	141.7(3)
C(11)-Co(1)-N(2)	91.0(3)	N(13)-Mn(1)-O(1W)	92.0(2)	O(2W)-Mn(1)-N(15)	89.8(2)
C(14)-Co(1)-N(2)	89.8(3)	N(13)-Mn(1)-N(14)	72.4(3)	N(16)-Mn(1)-N(15)	144.0(3)
N(1)-Co(1)-N(2)	82.1(3)	O(1W)-Mn(1)-N(14)	91.1(2)	N(17)-Mn(1)-N(15)	71.6(3)
C(26)-Co(2)-C(27)	88.9(3)	N(13)-Mn(1)-O(2W)	86.6(2)		
C(26)-Co(2)-C(25)	88.3(3)	O(1W)-Mn(1)-O(2W)	178.2(2)		
C(27)-Co(2)-C(25)	88.1(3)	N(14)-Mn(1)-O(2W)	87.4(2)		

CONCLUSIONS

The reaction between coordinatively unsaturated preformed dicobalt(II) and mononuclear manganese(II) complexes with the diamagnetic $\text{PPh}_4[\text{Co}^{\text{III}}(\text{AA})(\text{CN})_4]$ (AA = phen, bipy) metalloligand resulted into the formation of two new compounds: a neutral tetranuclear complex, with formula $\{[\text{Co}^{\text{II}}_2(\text{L})(\text{MeOH})_2][\text{Co}^{\text{III}}(\text{phen})(\text{CN})_4]_2\} \cdot 2\text{H}_2\text{O} \cdot 0.5\text{MeOH}$ (**1**) and a complex cation - complex anion compound of formula $[\text{Mn}^{\text{II}}(\text{MAC})(\text{H}_2\text{O})_2][\text{Co}^{\text{III}}(\text{bipy})(\text{CN})_4]_2 \cdot 3\text{H}_2\text{O}$ (**2**). In the crystal packing of both compounds extensive supramolecular H-bonding networks can be found. Variable-temperature magnetic measurements of **1** show the occurrence of a moderately strong antiferromagnetic interaction between the high-spin cobalt(II) ions which is mediated by the double phenoxido bridges.

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