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A two-dimensional honeycomb coordination network based on fused triacontanuclear heterometallic {Co₁₂Mn₁₈} wheels†

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An unprecedented two-dimensional honeycomb network based on fused triacontanuclear heterometallic wheels of 3.4 nm, {[Co₂(Mn₃O)(N₃)₂(pic)₆(NO₃)][−]]₆ (Hpic = picolinic acid), has been assembled. The hexagonal {Co₁₂Mn₁₈} wheel motif is composed of six oxo-centered {Mn₃} trinuclear and six {Co₂} dinuclear moieties acting as nodes and linkers, respectively. The paramagnetic properties of this compound observed down to 1.8 K result from the competition of Mn··Mn, Mn··Co and Co··Co interactions in combination with spin–orbit coupling and single-ion behavior of the Co(II) centers.

High-nuclearity complexes of paramagnetic 3d metal ions attract significant interests due to their intriguing geometrical characteristics (large size, high symmetry, aesthetically pleasing shapes and architectures) and fascinating physical properties.¹ As a subgroup of these complexes, polynuclear wheels have been extensively studied for their single-molecule magnet (SMM) properties (induced by the combination of their large spin ground state and an easy-axis magnetic anisotropy)^{1a,e,2} but also as model systems for spin frustration and quantum effects or as candidates for quantum-information processing (QIP).³ In particular antiferromagnetically coupled heterometallic wheels (AF-wheels) have recently gained attention due to their potential non-diamagnetic ground state that could be used as “qubit” in QIP devices.⁴ For example, Winpenny *et al.* have reported {Cr₇M} heterometallic AF-wheels for a coherent manipulation of the electron spin.⁵ Another crucial consideration for carrying out future quantum computation with these types of complexes is the control of the exchange interactions between these wheels, which depends partially on the nature of their connectivity. Therefore coordination networks of heterometallic

AF-wheel units may be nice systems to probe the effects of the inter-molecular interactions on the intrinsic properties of these complexes. The majority of the reported heterometallic wheels are discrete and small species,⁶ and only a few wheel-based coordination networks have been documented so far.⁷ No obvious and definite strategy has been established to synthesize these extended coordination architectures, and most of the approaches rely on serendipity. Therefore the synthesis of these polynuclear wheels and their derivative coordination networks remains a great synthetic challenge.

Serendipitous self-assembly is a well-used “bottom up” approach for elaborating coordination architectures, which often gives unexpected and exciting results.⁸ In this self-assembly approach, the key step is always the judicious selection of the organic ligand to stabilize polynuclear wheels^{1g,2c,9} and even in some cases wheel-based coordination networks.^{7f–h,10} In most of the examples, the bridging ligands possess N and/or O donor atoms,^{1a,5b,7g,h,11} and alkali metal ions assist the assembling of the wheels, which can also be considered as coordinating metallocrowns.^{7h,12} Herein we report a unprecedented trimetallic two-dimensional coordination network, Na[Co₃(Mn₃O)(pic)₆(N₃)₃(NO₃)₂] (**1**), which consists of fused hexagonal triacontanuclear heterometallic {[Co₂(Mn₃O)(N₃)₂(pic)₆(NO₃)][−]]₆ wheels of 3.4 nm separated by interlayer Na ions. The elementary building units are oxo-centered {Mn₃} trinuclear and {Co₂} dinuclear moieties, which are further assembled by picolinate ligands to create calixarene-like hydrophilic sites occupied by the sodium cations. Interestingly, this compound can be viewed as a coordination assembly of the so-far largest cobalt–manganese wheel.

Compound **1** was solvothermally obtained as single-crystals in a 12 ml Teflon-lined stainless steel container in high yield (*ca.* 76%) by treatment of a mixture of Co(NO₃)₂, Mn(CH₃COO)₂, picolinic acid and NaN₃ in ethanol at 140 °C.† It is worth mentioning that similar reactions by using a single transition metal precursor were unsuccessful. The purity of **1** was confirmed by elemental analysis, infra-red spectroscopy as well as by powder X-ray diffraction patterns (Fig. S1, ESI†). Single-crystal X-ray diffraction analysis reveals that **1** crystallizes in the *R*3̄ trigonal space group and the asymmetric unit contains only one Co, one Mn, one Na,

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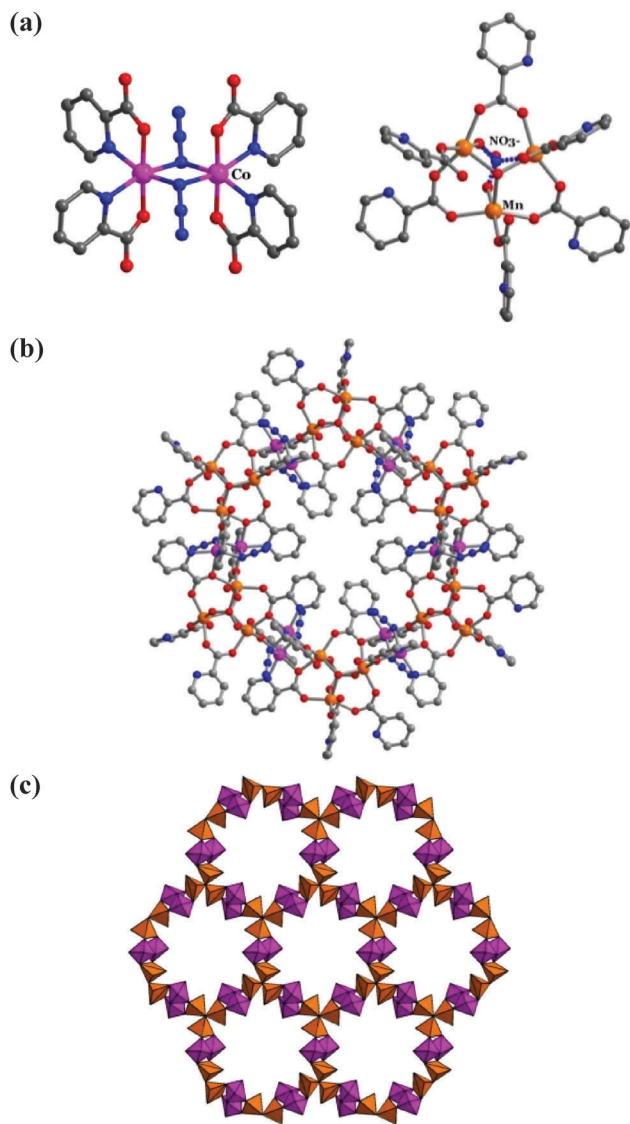


Fig. 1 (a) Ball and stick view of the $[\text{Co}_2(\text{pic})_4(\text{N}_3)_2]^{2-}$ and $[\text{Mn}_3\text{O}(\text{pic})_6(\text{NO}_3)]^{3-}$ units in **1**; (b) view of a triacontanuclear heterometallic $\{[\text{Co}_2(\text{Mn}_3\text{O})(\text{N}_3)_2(\text{pic})_6(\text{NO}_3)]^-\}_6$ wheel motif observed in **1** with dimensions of 3.2×0.8 nm and a hydrophobic inner diameter of 0.6 nm; (c) polyhedral-type view of the hexagonal network of $\{\text{Co}_2\text{Mn}_2\}_6$ icositetranuclear rings. The Co and Mn polyhedra are shown in purple and brown colors, respectively. Color code: Co purple, Mn orange, O red, N blue, and C grey. Hydrogen and Na atoms have been omitted for clarity.

one $\mu_3\text{-O}$, an azido anion, two pic^- ligands and two nitrate groups (Fig. S2, ESI†).§ The Na cation and two nitrates are located on a threefold axis, which implies disordered nitrate anions. The Co(II) site possesses a distorted octahedral coordination sphere occupied by two azido groups in *cis* positions, two N and two O atoms from two N,O-chelating picolinate ligands. The Co–X (X = O, N) bond lengths fall between 2.058(6) and 2.173(7) Å with an average Co–X distance of 2.110 Å. Two $\{\text{Co}(\text{pic})_2\}$ moieties are connected by a double $\mu_{1,1}$ -azido bridge to form the dinuclear $[\text{Co}_2(\text{pic})_4(\text{N}_3)_2]^{2-}$ unit with a short Co···Co distance of 3.159 Å (Fig. 1a). The Mn(II) site adopts a strongly distorted octahedral geometry, coordinated by three carboxylate O atoms, one nitrate O atom, one $\mu_3\text{-O}$ and

one azido anion. The Mn–O bond lengths are in the 2.147–2.251 Å range. The coordinating N atom from the azido anion is only weakly interacting with the Mn metal ion with a long Mn–N distance of 2.485 Å. The average Mn–X bond length is thus relatively large at 2.249 Å. In agreement with the d^5 and d^7 electronic configuration of the Mn(II) and Co(II) metal ions and their usual coordination radius, the average Mn–X distance is larger than the Co–X one. In addition, the coexistence of Mn(II) and Co(II) metal ions in **1** was also confirmed by EDS (Fig. S3, ESI†) and supported by magnetic measurements (*vide infra*). Meanwhile, the +2 oxidation state of the Mn ion was determined by bond-valence sum (BVS) calculation (Table S3, ESI†),¹³ charge-balance consideration and inspection of the coordination sphere.^{2b,14} Three Mn metal ions and six picolinate ligands assemble around a central $\mu_3\text{-O}$ atom to form a 3-fold oxo-centered $[\text{Mn}_3\text{O}(\text{pic})_6]^{2-}$ unit with a unique Mn···Mn distance of 3.587 Å (Fig. 1a). This $[\text{Mn}_3\text{O}(\text{pic})_6]^{2-}$ moiety has at the same time available coordination sites occupied by one nitrate ion and oxygen donor atoms (from the picolinate ligands), which coordinate a sodium cation capped by an additional nitrate. The NO_3^- and $\text{Na}(\text{O}_3\text{N})$ groups are lying on each side of the $[\text{Mn}_3\text{O}(\text{pic})_6]^{2-}$ moiety along the three-fold axis to form a $[\text{NaMn}_3\text{O}(\text{pic})_6(\text{NO}_3)_2]^{3-}$ unit as shown in Fig. S4 (ESI†). Each $[\text{NaMn}_3\text{O}(\text{pic})_6(\text{NO}_3)_2]^{3-}$ unit is linked to three $[\text{Co}_2(\text{pic})_4(\text{N}_3)_2]^{2-}$ moieties *via* sharing oxygen atoms of picolinate ligands to form a two-dimensional neutral honeycomb coordination network, $\text{Na}[\text{Co}_3(\text{Mn}_3\text{O})(\text{pic})_6(\text{N}_3)_3(\text{NO}_3)_2]$, that can be seen as resulting from the fusion of triacontanuclear heterometallic $\{[\text{Co}_2(\text{Mn}_3\text{O})(\text{N}_3)_2(\text{pic})_6(\text{NO}_3)]^-\}_6$ wheels (Fig. 1b and Fig. S5, ESI†). Each wheel unit has dimensions of 3.2×0.8 nm and a hydrophobic inner diameter of 0.6 nm. This 2D network can also be described as an inorganic hexagonal layer of $\{\text{Co}_2\text{Mn}_2\}_6$ icositetranuclear rings (Fig. 1c) with picolinate ligands projecting inward the ring motifs as well as on both sides of the inorganic sheet. The center of each $\{\text{Co}_2\text{Mn}_2\}_6$ icositetranuclear ring is occupied by six picolinate ligands to create a small hydrophobic central cavity. More interestingly, the three interlayer pic^- groups in combination with $[\text{Mn}_3\text{O}]^{4-}$ units create multiple calixarene-like hydrophilic cavities (Fig. S6, ESI†) pointing to both sides of the sheets. The three carboxylate oxygen atoms from these cavities form an equilateral triangle with an O···O distance of 3.26 Å, which chelate a Na^+ ion. Due to the smaller O···O distance, the Na^+ site is non-coplanar with the three oxygen atoms and is lying above the mean oxygen plane at 1.106 Å.^{7b}

The magnetic susceptibility measurements of **1** were performed between 1.85 and 300 K (Fig. 2). At room temperature, the χT product is $6.7 \text{ cm}^3 \text{ K mol}^{-1}$, which is in good agreement with the presence of one Mn^{II} ($C = 4.375 \text{ cm}^3 \text{ K mol}^{-1}$) and one Co^{II} ($S = 3/2$, $C = 2.325 \text{ cm}^3 \text{ K mol}^{-1}$ and $g = 2.22$) metal ions.¹⁵ Upon decreasing the temperature, the χT product decreases gradually until 10 K and then declines more rapidly at lower temperatures to reach $3.2 \text{ cm}^3 \text{ K mol}^{-1}$ at 1.85 K. The complicated nature of the 2D coordination network, the many different magnetic pathways between Mn^{II} and Co^{II} magnetic centers and also the intrinsic Co^{II} paramagnetism (strongly influenced by strong spin–orbit coupling) preclude a detailed analysis of the magnetic



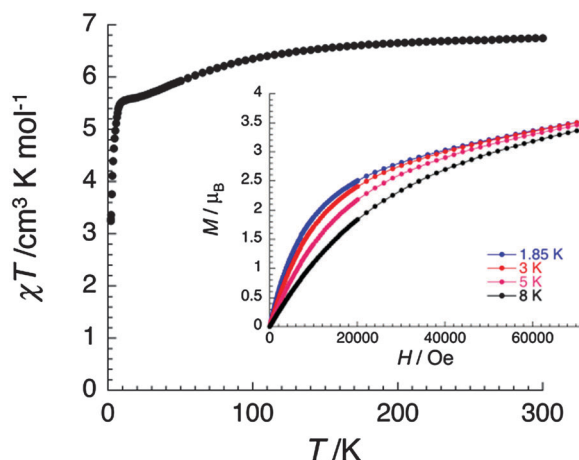


Fig. 2 Temperature dependence of the χT product at 1000 Oe (where χ is the molar magnetic susceptibility equal to the ratio between the magnetization and the applied magnetic field, M/H , per mole of {CoMn} pair) between 1.85 and 300 K for a polycrystalline sample of **1**. Inset: M vs. H plot for **1** between 1.85 and 8 K at magnetic fields between 0 and 7 T with sweep-rates of 100–200 Oe min^{-1} . The solid line is a guide for the eye.

properties and thus the development of a convincing magnetic model. Nevertheless, the nonzero plateau (residual paramagnetism) observed at around 10 K in the χT vs. T data (Fig. 2) is clearly highlighting the non-compensation of the magnetic centers of the 2D coordination network.^{5b,16} The field dependence of magnetization measured below 8 K (Fig. 2 inset and Fig. S7, ESI†) is also informative. The increase of the magnetization at high field without clear saturation, even at 1.8 K and under 7 T, confirms the expected presence of the Co^{II} magnetic anisotropy^{1b,10a,16} and the possible influence of low-lying excited states induced by weak antiferromagnetic interactions. It is also worth mentioning that 1.85 K magnetization reaches 3.5 μ_B at the highest field of 7 T, that is far below the expected saturation value for one Co^{II} and one Mn^{II} metal ions revealing the presence of operative antiferromagnetic interactions in the material. Even if the M vs. H data do not exhibit any hysteresis effect (at the field sweep-rates of 50–400 Oe min^{-1} used in commercial magnetometers), the magnetization dynamics for **1** has also been investigated by ac susceptibility measurements (Fig. S8, ESI†). In our temperature (1.8–300 K) and ac frequency (0.1–10 000 Hz) experimental windows, it was impossible to detect a significant out of phase ac signal, excluding the possibility of a magnet-type behavior in this system above 1.8 K.

In summary, an unprecedented two-dimensional honeycomb paramagnetic network based on fused triacontanuclear heterometallic nanometric wheels, $\{[\text{Co}_2(\text{Mn}_3\text{O})(\text{N}_3)_2(\text{pic})_6(\text{NO}_3)]\}_6$, has been successfully synthesized and structurally characterized. The oxo-centered $\{\text{Mn}_3\}$ trinuclear and $\{\text{Co}_2\}$ dinuclear units are respectively located at the corners and edges of these hexagonal wheels. Importantly, the successful synthesis of **1** not only confirms the feasibility of synthesizing novel multimetallic complexes through a judicious choice of appropriate ligands and different metal ions but also provides an interesting strategy to develop the synthesis of wheel-based systems for potential

QIP applications. In addition, the calixarene-like hydrophilic active sites could be potentially used for ion recognition or exchange. Therefore, synthetic strategies to selectively substitute the Na^+ ions but also the Co^{2+} and/or Mn^{2+} metal ions with other species are currently underway in our laboratory.

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Notes and references

‡ Synthesis of $\text{Na}[\text{Co}_3(\text{Mn}_3\text{O})(\text{pic})_6(\text{N}_3)_3(\text{NO}_3)_2]$ (**1**). A suspension of $\text{Co}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.163 g, 0.56 mmol), $\text{Mn}(\text{CH}_3\text{COO})_2$ (0.100 g, 0.54 mmol), picolinic acid (0.086 g, 0.7 mmol), and NaN_3 (0.052 g, 0.8 mmol) in ethanol (5 ml) was sealed in a 12 ml Teflon-lined stainless steel container that was heated to 140 °C and held at this temperature for 96 hours. After cooling to room temperature, red columnar single crystals of **1** (76%) were obtained. Elemental analysis (%). Anal. Calcd for $\text{C}_{36}\text{H}_{24}\text{Co}_3\text{Mn}_3\text{N}_{17}\text{NaO}_{19}$: C, 31.76; H, 1.77; N, 17.46. Found: C, 31.88; H, 1.53; N, 17.53. IR (KBr): 3433s, 2029m, 1639s, 1377s, 1124w, 1038w, 837w, 761w, 700w.

§ Crystal data for **1**: $\text{C}_{36}\text{H}_{24}\text{Co}_3\text{Mn}_3\text{N}_{17}\text{NaO}_{19}$, Trigonal, space group $R\bar{3}a$ = 17.343(7) Å, c = 31.6652(19) Å, V = 8248.2(7) Å³, T = 293(2) K, Z = 6, ρ = 1.714 g cm^{-3} , (R_{int} = 0.0329), R_1 = 0.0883, wR_2 = 0.2323 (for $I > 2\sigma(I)$), (GOF = 1.064).

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