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Three 3-Amino-1,2,4-Triazole-Based Magnetic Complexes Incorporated with Different Carboxylate-Containing Coligands: Synthesis, Structures, and **Magnetic Properties**

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Abstract. Three 3-amino-1,2,4-triazole (atz)-based paramagnetic complexes, $[Mn(atz)(pa)]_n$ (1), $\{[Mn(atz)_{1.5}(hip)] \cdot H_2O\}_n$ (2), and $[Mn(H_2O)_2(atz)_2(nb)_2]$ (3) $(H_2pa = o-phthalic acid, H_2hip =$ 5-hydroxylisophthalic acid, and Hnb = p-nitrobenzoic acid) were prepared by introducing different carboxylate-containing aromatic coligands, and structurally and magnetically characterized. Helical Mn^{II}-atz and bent Mn^{II}-pa²⁻ chains are crosslinked by sharing the same metal sites to generate a honeycomb-shaped framework of 1. The undulated Mn^{II}-atz layers constructed from 22-member metallomacrocycles are periodically supported by ditopic hip²⁻ ligands to lead to a

Introduction

Recently, the design and assembly of molecule-based magnetic materials built from suitable organic magnetic bridges and inorganic paramagnetic metal ions are of intense interest in the fields of coordination and material chemistry.^[1-3] Acting as a large family of five-member aza-heterocyclic organics, triazole and the diverse derivatives have gradually becoming one of the superior mediators, because lots of binary transition metal ion-triazolate and ternary paramagnetic ion-triazolatecarboxylate magnetic systems with interesting magnetic behavior have been generated by optimized synthetic conditions.^[3–16] The rich and varied coordination characteristics,^[4] the asymmetric tridentate bridging mode^[7,8] as well as the well-suited distance by cyclic triazolyl group have been strongly recognized as the main factors for efficient antiferromagnetic superexchange between the nearest spin carriers. Furthermore, the exocyclic substitutes of the triazolate deriva-

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pillared-layer structure of 2. In contrast, complex 3 is a centrosymmetric mononuclear entity, which is assembled into a three-dimensional supramolecular network by abundant hydrogen-bonding interactions. The structural difference of 1-3 is significantly due to the combinations of the flexible coordination modes adopted by the mixed atz and carboxylate groups. Weak and comparable antiferromagnetic couplings are observed in the nearest neighbors of 1-3, which are cooperatively transmitted either by short carboxylate and/or atz heterobridges or by weak non-covalent interactions.

tives with end-on coordination capacity, such as mono- and/or di-amino, carboxylato, as well as mercapto groups, can also synergically assist the structural diversity and magnetic interactions either by coordination with spin carriers or by weak non-covalent interactions.^[5,17] Additionally, polycarboxylate moiety coming from the separate coligand can not only modify the magnetic phenomena by conformation-dependent magnetic couplings but also essentially govern the overall connectivity of the targeted three-dimensional (3D) frameworks by the number and position effects.[7,8]

On the other hand, different transition metal ions with diverse magnetic nature also play important roles for the resulting interesting magnetic behavior, in which the variable coordination polyhedra, the spin-orbit coupling, as well as the single-ion anisotropy of the paramagnetic centers have become the most important factors. Up to date, lots of 3D robust Co^{II}and Cu^{II}-containing magnetic frameworks with mixed triazolate and polycarboxylate mediators have been investigated by changing different paramagnetic centers or by subtle combination of mixed heterobridges, which exhibit interesting secondary building units, framework connectivity and promising spin-glassy, spin-flop, as well as spin-frustration phenomena.^[6–8,13] However, to the best of our knowledge, only a few 3-amino-1,2,4-triazole (atz)-based manganese(II) complexes have been investigated by far.[14,18-20]

Herein, to continue our interest in the magnetostructural correlations of the mixed triazole-carboxylate-based magnetic systems,^[7,8,16] three carboxylate-modified coligands, ophthalic acid (H₂pa), 5-hydroxylisophthalic acid (H₂hip), and

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p-nitrobenzoic acid (Hnb), were selected as secondary mediators to react with paramagnetic Mn^{II} ions and atz molecules, respectively. The special interest for introducing these coligands is that they have different functionality and molecular topology, and can hopefully direct the structure and magnetism of the targeted complexes. As a result, three magnetic samples, a honeycomb-like 3D framework 1, a pillared-layer coordination network 2, as well as a centrosymmetric mononuclear molecule 3, were successfully generated through slow evaporation method at room temperature. The three complexes were structurally and magnetically characterized. Structural determinations reveal that the variable structural motifs and dimensionality of 1-3 are essentially governed by the flexible binding fashions of the mixed ligands with the octahedral Mn^{II} ion. Weak antiferromagnetic interactions are transmitted in the nearest neighbors of the spin carriers mainly by the cooperative carboxylate and triazolyl heterobridges or through noncovalent weak interactions.

Results and Discussion

Syntheses and FT-IR Spectroscopy

Complexes 1–3 can be readily obtained by conventional evaporation method at room temperature, which is apparently due to the suitable solubility of the reactant mixture in mixed methanol/water medium. Notably, two factors, the inorganic anions of the metal salts (NO₃⁻ for both 1 and 2 and ClO₄⁻ for 3) and the mixed medium with pH = 6, were found to be more essential for the growth of the targeted crystalline samples. In the IR spectra, a weak absorption located at 3446 cm⁻¹ for 1 can be assigned to the stretching vibration of N–H,^[21] suggest-

Table 1. Crystal data and structure refinement parameters for 1-3.

ing the presence of an amino group of the atz ligand. An obviously broad band centered at 3422 cm^{-1} for **2** indicates the presence of water molecule, which probably masks the weak absorption for the N–H of the amino group. A weak band at 3462 cm^{-1} and a strong one at 3366 cm^{-1} in **3** should be ascribed to the stretching vibrations of N–H and O–H, respectively, revealing the coexistence of the amino group of atz and water molecule.

As compared with the free organic acids, the disappearance of a characteristic band at 1686 cm⁻¹ for **1**, at 1712 cm⁻¹ for **2**, and at 1703 cm⁻¹ for **3** is an indicative of the full deprotonation of H₂pa, H₂hip, and Hnb, respectively. The strong absorptions appearing at 1635, 1559, and 1406 cm⁻¹ in **1** are ascribed to the asymmetric (v_{as}) and symmetry stretching vibrations (v_s) of carboxylate groups. For the latter two complexes, they are located at 1650, 1557, 1508, and 1383 cm⁻¹ for **2** and at 1613 and 1578 cm⁻¹ as well as 1382 and 1343 cm⁻¹ for **3**. The different separations ($\Delta v = v_{as} - v_s$) suggest the coexistence of the terminally monodentate and bridging bidentate modes of the carboxylate groups in **1**–**3**.^[21] Thus, the IR results are in agreement with the single-crystal X-ray structural analyses.

Structural Description of $[Mn(atz)(pa)]_n$ (1)

Complex 1 crystallizes in the rhombohedral $R\bar{3}$ space group (Table 1), exhibiting a microporous honeycomb-like 3D framework constructed from the interconnection of helical Mn^{II}-atz and bent Mn^{II}-pa²⁻ chains. The asymmetric unit of 1 contains one unique Mn^{II} atom, one neutral atz ligand, and one doubly deprotonated pa²⁻ anion. As illustrated in Figure 1a, the sole Mn^{II} ion in 1 is hexacoordinate in a distorted octahedral coor-

	1	2	3
Formula	$C_{30}H_{24}Mn_3N_{12}O_{12}$	$C_{11}H_{12}MnN_6O_6$	$C_{18}H_{20}MnN_{10}O_{10}$
Fw	909.43	379.21	591.38
Crystal system	rhombohedral	monoclinic	triclinic
Space group	RĪ	C2/c	$P\bar{1}$
a /Å	28.801(8)	18.062(4)	7.3540(11)
b /Å	28.801(8)	7.7841(16)	7.5884(11)
c /Å	7.473(2)	19.994(4)	11.922(3)
a /°	90	90	91.739(3)
β /°	90	94.236(6)	96.303(3)
γ /°	120	90	118.480(2)
V/Å ³	5368(2)	2803.3(11)	578.65(19)
Z	6	8	1
$D_c / \text{g-cm}^{-3}$	1.688	1.740	1.697
μ /mm ⁻¹	1.123	0.986	0.650
F(000)	2754	1496	303
Limiting indices	$-34 \le h \le 33$	$-17 \le h \le 21$	$-8 \le h \le 8$
	$-28 \le k \le 34$	$-9 \le k \le 9$	$-8 \le k \le 9$
	$-6 \le l \le 8$	$-23 \le l \le 18$	$-10 \le l \le 14$
Data / restraints / params	2067/0/172	2477 / 12 / 233	2020 / 0 / 178
R _{int}	0.0586	0.0510	0.0167
GoF on F^2	1.070	1.055	1.071
R_1^{a} , wR_2^{b} $[I > 2\sigma(I)]$	0.0386, 0.0953	0.0427, 0.0951	0.0328, 0.0755
R_1 , wR_2 [all data]	0.0517, 0.1024	0.0632, 0.1018	0.0392, 0.0799
Residuals /e·Å ⁻³	1.201, -0.385	0.622, -0.484	0.245, -0.313

a) $R_1 = \Sigma ||F_0| - |F_c|| / \Sigma |F_0|$. b) $wR_2 = [\Sigma w (|F_0^2| - |F_c^2|)^2 / \Sigma w |F_0^2|^2]^{1/2}$.



Figure 1. (a) Local coordination environments of Mn^{II} ion in **1** (hydrogen atoms are omitted for clarity. Symmetry codes: A = 1 - x, 2 - y, 1 - z; B = 1 - x, 2 - y, 2 - z, C = y - x + 1/3, 3/5 - x, z - 1/3); (b) Bent and helical chains of **1** constructed from Mn^{II} ions, carboxylate groups and μ -N2,N4-atz ligands; (c) 3D honeycomb-like framework of **1** formed by the interconnected Mn^{II} -pa²⁻ and Mn^{II} -atz chains.

dination arrangement completed by four carboxylate oxygen donors from three separate pa^{2-} coligands and two triazolyl nitrogen atoms from two neutral atz molecules. The Mn–O and Mn–N separations are between 2.108(2) and 2.268(3) Å (Table 2), which are comparable with those Mn^{II}-containing complexes with mixed carboxylate and tri-/tetrazolyl ligands.^[14,16]

Table 2. Selected bond lengths /Å and angles /° for 1.

Mn(1)-O(2)#1	2.108(2)	Mn(1)-N(3)#3	2.199(3)
Mn(1)-O(4)#2	2.155(2)	Mn(1)-N(2)	2.268(3)
Mn(1)–O(3)	2.182(2)	Mn(1)–O(1)	2.187(2)
O(2) ^{#1} -Mn(1)-O(4) ^{#2}	90.54(9)	$O(2)^{#1}$ -Mn(1)-N(2)	177.83(10)
O(2) ^{#1} -Mn(1)-O(3)	94.32(9)	O(4)#2-Mn(1)-N(2)	88.47(9)
$O(4)^{#2}-Mn(1)-O(3)$	91.67(9)	O(3)-Mn(1)-N(2)	87.64(9)
O(2) ^{#1} -Mn(1)-O(1)	93.99(9)	O(1)-Mn(1)-N(2)	87.13(9)
$O(4)^{#2}-Mn(1)-O(1)$	173.80(9)	$N(3)^{#3}-Mn(1)-N(2)$	84.32(10)
O(3)-Mn(1)-O(1)	83.78(8)	O(3)-Mn(1)-N(3)#3	171.96(9)
O(2)#1-Mn(1)-N(3)#3	93.72(10)	O(1)-Mn(1)-N(3)#3	95.83(9)
O(4) ^{#2} -Mn(1)-N(3) ^{#3}	88.09(9)		

Symmetry codes: #1 1 - x, 2 - y, 1 - z; #2 1 - x, 2 - y, 2 - z; #3 $y - x + \frac{1}{3}$, $\frac{3}{5} - x$, $z - \frac{1}{3}$.

As shown in Figure 1b, pairs of symmetry-related pa^{2-} ligands present the two adjacent carboxylate groups to link the neighboring Mn^{II} ions into a bent Mn^{II}-pa²⁻ chain running along the crystallographic *c* axis, in which the both carboxylate groups are in a bidentate bridging *anti*, *syn* conformation (μ *anti*, *syn*-COO⁻). By contrast, the atz ligand in **1** adopts a bridging μ -N2,N4-bridging mode to infinitely extend the adjacent Mn^{II} ions into a helical chain also running along the crystallographic *c* axis (Figure 1b). Notably, the independent Mn^{II}- atz chains are arranged in an alternating left- and right-handed helical manner to lead to a racemic nature of **1**. The Mn^{II}•••Mn^{II} separations bridged by μ -*anti*, *syn*-COO⁻ and μ -N2,N4-atz mediators are 4.5999(9), 4.9436(1), and 6.5525(13) Å. Obviously, the effective magnetic coupling in **1** is essentially dominated in the bent Mn^{II}-pa²⁻ chain. These separated Mn^{II}-pa²⁻ and Mn^{II}-atz chains are interwoven together by sharing the crystallographically unique Mn^{II} ion, generating an overall 3D microporous framework of **1** (Figure 1c). The solvent accessible void fraction is 9.5% calculated by PLATON.^[22]

Structural Description of $\{[Mn(atz)_{1.5}(hip)] \cdot H_2O\}_n$ (2)

Complex **2** is a 3D pillared-layer framework constructed from cationic Mn^{II} -atz layers and anionic hip^{2-} pillars, exhibiting a 6-connected α -*P*o-type topological structure. There is one crystallographically independent Mn^{II} atom, one and a half neutral atz ligands, one doubly deprotonated hip^{2-} anion, and one disordered lattice water molecule in the asymmetry unit of **2**. As shown in Figure 2a, the unique Mn^{II} atom in **2** is in an O_3N_3 donor set completed by three individual triazolyl moieties from three neutral atz molecules and three carboxylate groups from three different hip^{2-} ligands, assuming a distorted octahedral coordination arrangement with the Mn–O distances slightly shorter than those of Mn–N separations (Table 3).

One atz ligand with a crystallographic twofold axis symmetry in **2** adopts a μ -N1,N2-bridging mode to aggregate two adjacent Mn^{II} ions into a dimeric subunit with the intermetallic distance of 4.0151(9) Å. To the best of our knowledge, such a bidentate binding mode of atz ligand has been infrequently





Figure 2. (a) Local coordination environments of Mn^{II} ion in **2** (hydrogen atoms are omitted for clarity. Symmetry codes: A = x, y, 1/2 –z; B = x, y, z – 1; C = – x, 1 – y, 1 – z); (b) 2D layer of **2** with dinuclear subunits extended by μ -N2,N4-atz connectors; (c) 3D pillared-layer framework and the topological denotation of **2**.

Table 3. Selected bond lengths /Å and angles /° for 2.

Mn(1) = O(1)	2.123(3)	$Mn(1) - O(2)^{\#1}$	2.172(3)
$Mn(1)-O(4)^{#2}$	2.199(3)	Mn(1) - N(5)	2.236(3)
Mn(1)–N(3)	2.233(3)	$Mn(1)-N(2)^{\#3}$	2.268(3)
O(1)-Mn(1)-O(2) ^{#1}	94.57(10)	O(1)-Mn(1)-N(5)	99.57(11)
O(1)-Mn(1)-O(4) ^{#2}	90.03(10)	$O(2)^{\#1}-Mn(1)-N(5)$	94.12(11)
$O(2)^{#1}-Mn(1)-O(4)^{#2}$	175.32(9)	O(4)#2-Mn(1)-N(5)	85.96(11)
O(1)-Mn(1)-N(3)	172.86(11)	N(3)-Mn(1)-N(5)	87.56(12)
$O(2)^{\#1}-Mn(1)-N(3)$	85.37(11)	O(1)-Mn(1)-N(2)#3	88.31(11)
$O(4)^{#2}-Mn(1)-N(3)$	89.95(11)	$O(2)^{\#1}-Mn(1)-N(2)^{\#3}$	89.53(10)
N(3)-Mn(1)-N(2)#3	84.55(12)	$O(4)^{#2}-Mn(1)-N(2)^{#3}$	89.72(11)
N(5)-Mn(1)-N(2)#3	171.01(12)		

Symmetry codes: #1 *x*, *y*, 1/2 –*z*; #2 – *x*, 1 – *y*, 1 – *z*; #3 1/2 –*x*, *y* – 1/2, 1/2 –*z*.

observed in the atz-based metal complexes. Each dimeric Mn_2^{II} core in **2** is further extended by four μ -N2,N4-atz ligands, leading to a 22-member metallomacrocycle-based layer made from six Mn^{II} ions, two μ -N1,N2- and four μ -N2,N4-atz ligands (Figure 2b). The intermetallic separation by the μ -N2,N4-atz linker is 6.5630(11) Å, considerable longer than that held by the μ -N1,N2-atz molecule.

Each wave-like layer in **2** is periodically supported by the coordination of the carboxylate groups of hip^{2–} pillars with the interlayer metal ions in bidentate bridging and monodentate fashions, leading to a 3D pillared-layered framework of **2** with the interlayer separation of 10.0910(21) Å (Figure 2c). Topologically, each dinuclear unit of **2** aggregated by μ -N1,N2-atz can be considered as a node, and the hip^{2–} and μ -N2,N4-atz ligands can be served as two different kinds of ditopic connectors. Thus, the 3D coordination polymer of **2** can be predi-

gested into a 6-connected α -*P*o-type topological structure (Figure 2c).

Structural Description of $[Mn(H_2O)_2(atz)_2(nb)_2]$ (3)

Complex **3** is a centrosymmetric mononuclear molecule, which is assembled into a 3D supramolecular network by abundant N–H···O hydrogen-bonding interactions. The unique Mn^{II} atom in **3** is in an inversion center, surrounded by two axial carboxylate oxygen atoms from a pair of symmetry-related nb⁻ anion and four equatorial N₂O₂ donors from pairs of triazolyl groups of atz and terminal water molecules, adopting axially compressed octahedral coordination arrangement with axial Mn–O_{carboxylate} separations 0.08 Å shorter than those of equatorial Mn–O_{aqua} and Mn–N bonds (Table 4)

Table 4. Selected bond lengths /Å and angles /° for 3.

Mn(1)–O(1)	2.1735(14)	Mn(1)–N(3)	2.2460(18)
Mn(1)-O(5)	2.2509(15)		
O(1)-Mn(1)-N(3) ^{#1}	90.45(6)	N(3)-Mn(1)-O(5) ^{#1}	88.87(6)
O(1)-Mn(1)-N(3)	89.55(6)	O(1)-Mn(1)-O(5)	88.24(5)
O(1)-Mn(1)-O(5) ^{#1}	91.76(5)	N(3)–Mn(1)–O(5)	91.13(6)
			-

Symmetry codes: #1 1 -x, 2 -y, 1 -z.

Rather than serving as μ -N2,N4 and/or μ -N1,N2-bridging coordination modes in **1** and **2**, the neutral atz ligand in **3** only presents the N4 donor site to coordinate with Mn^{II} atom in a monodentate fashion. Additionally, the imino group of atz ligand can act as a typical hydrogen-bond donor to produce two N–H···O hydrogen-bonding interactions with the coordinated water molecule and free nitro group of nb⁻ anion (Table S1,



Figure 3. (a) Mononuclear structure of 3 (hydrogen atoms are omitted for clarity. Symmetry codes: A = 1 -x, 2 -y, 1 -z.); (b) 2D supramolecular layer of 3 generated by hydrogen bond interactions; (c) 3D stacking pattern of 3 formed by non-covalent contacts.

Supporting Information), which connects the discrete monouclear molecules into a coplanar supramolecular layer (Figure 3b). These non-covalent layers of **3** can be further stacked into a non-covalent 3D network also by inter-layer N–H···O contacts between the amino moiety of atz ligand and nitro group of nb⁻ anion (Figure 3c, Table S1).

TGA and PXRD of 1-3

Thermogravimetric analyses (TGA) of 1-3 were carried out to evaluate their compositional stability (Figure 4). As a result, complex 1 can be thermally robust up to 320 °C, and is followed by a continuous weight-loss process between 320 and 503 °C for the decomposition of the mixed ligands. The remaining residue of the complex is MnO (exp. 22.7%, calcd. 23.4%). In contrast, 2 exhibits a continuous two-step weightloss stage from 50 °C to 192 °C for the release of disordered lattice molecule and between 258 and 517 °C for the collapse of the pillared-layer framework. The final product of 2 above 517 °C is calculated to be MnO (exp. 18.3%, calcd. 18.7%). Complex 3 also displays a two-step weight-loss process beyond 120 °C. The first stage between 120 °C and 137 °C is due to the loss of two coordinated water molecules (exp. 6.4%, calcd. 6.1%). The second obvious weight-loss process that begins 224 °C and ends at 828 °C is ascribed to the removal of the mixed ligands. The remaining residue of the mononuclear molecule is MnO (exp. 11.9%, calcd. 12.0%). PXRD experiments were carried out for 1-3 to confirm their crystalline phase-purity. The experimental and computer-simulated PXRD

patterns of the two bulk samples (Figure S1, Supporting Information) are in good agreement with each other, indicating the phase purity of the as-synthesized products.



Figure 4. TG curves for 1–3.

Magnetic Properties

Variable-temperature (2–300 K) magnetic susceptibilities of **1–3** were measured under an applied field of 2.0 kOe. As shown in Figure 5a, the observed $\chi_M T$ value for per Mn^{II} unit of **1** (4.38 cm³·K·mol⁻¹) is consistent with the spin-only value (4.37 cm³·K·mol⁻¹) expected for one magnetically uncoupled





Figure 5. (a) Plots of $\chi_{\rm M}T$ and $\chi_{\rm M}^{-1}$ vs. T for 1–3. The solid lines correspond to the best least-square fit indicated in the text. (b) Isothermal magnetizations for 1–3 at 2.0 K.

Mn^{II} ion with S = 5/2 and g = 2.0. The $\chi_{\rm M}T$ product continuously decreases with the decreased temperature, suggesting that an antiferromagnetic coupling occurs in the nearest neighbors of **1**. The plot of $\chi_{\rm M}^{-1}$ vs. *T* above 10 K follows the Curie-Weiss law with $C = 4.68 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ and $\theta = -20.8 \text{ K}$. The negative θ value further confirms the antiferromagnetic interactions dominated between the neighboring Mn^{II} ions of **1**, which can be further evidenced by the field-dependent magnetization of **1** measured at 2.0 K increases linearly with the increasing fields, and gets to a maximum value $(1.2 N\beta)$ at 50 kOe, which is far from the saturation value of one Mn^{II} ion $(5.0 N\beta)$.

Magnetically, the Mn^{II}-pa²⁻ chain extended two carboxylate groups should be essentially dominated the superexchange interaction of **1** due to the relatively short intermetallic distance. The magnetic model of an infinite uniform chain can thus be used to fit the superexchange couplings, in which the molecular field approximation is introduced to evaluate the interchain magnetic interaction mediated by the μ -N2,N4-atz ligand.^[23] The molar magnetic susceptibility of **1** can be fitted by the following expressions Equation (1) and Equation (2):

$$\chi_{\text{chain}} = [N \ g^2 \beta^2 \ S \ (S+1)/(3kT)][(1+u)/(1-u)] \tag{1}$$

with
$$u = \operatorname{coth}[JS(S+1)/kT] - kT/[JS(S+1)]$$

 $\chi_{\rm M} = \chi_{\rm chain}/(1 - (2zJ'/N\beta^2 g^2)\chi_{\rm chain})$
(2)

The best least-squares fit of the theoretical equations to the experimental data led to g = 2.01, $J = -0.53 \text{ cm}^{-1}$, $zJ' = -0.11 \text{ cm}^{-1}$, and $R = 5.7 \times 10^{-4}$, where $R = \sum [(\chi_M T)_{obsd} - (\chi_M T)_{calcd}]^2/[(\chi_M T)_{obsd}]^2$. Obviously, the negative value for *J* confirms the antiferromagnetic interaction mediated by the two carboxylate bridges is compared with those previous reported Mn^{II}-containing complexes with double *syn-*, *anti*-COO⁻ mediators, [Mn₂(Hphth)₂(phen)₄](Hphth)₂·2H₂O (phth = phthalate and phen = 1,10-phenanthroline) with $J = -0.34 \text{ cm}^{-1[24]}$ and [Mn(μ -ClCH₂COO)₂(phen)]_n with $J = -0.89 \text{ cm}^{-1}$.^[25] The relatively weak zJ' component supports the weak interchain antiferromagnetic contact through μ -N2,N4-atz ligand.

The $\chi_{\rm M}T$ product for each Mn^{II}₂ unit of **2** is 8.61 cm³·K·mol⁻¹ at 300 K (Figure 5a), close to the theoretical value (8.74 cm³·K·mol⁻¹) for two isolated Mn^{II} ions with S = 5/2 and g = 2.0. The $\chi_{\rm M}T$ value of **2** is continuously decreases as the temperature decreases and reaches a minimum value of

1.11 cm³·K·mol⁻¹ at 2.0 K. The plot of $\chi_{\rm M}^{-1}$ vs. *T* above 10 K follows the Curie-Weiss law with C = 8.91 cm³·K·mol⁻¹ and $\theta = -7.60$ K. The negative Weiss constant θ suggest antiferromagnetic couplings between the nearest spin carriers in **2** that is transmitted by the mixed μ -N1,N2-atz and *syn*, *anti*-COO⁻ heterobridges. Analogous to **1**, the magnetization of **2** increases linearly with the increasing field at 2.0 K, and the value (5.4 N β) at 50 kOe is far from the saturation value for two Mn^{II} ions (10.0 N β , Figure 5b).

From the viewpoint of magnetostructural correlations, the magnetic interactions of **2** are significantly interacted with the 2D layer with $[Mn_2(\mu-N1,N2-atz)(syn, anti-COO^-)_2]$ subunit periodically extended by μ -N2,N4-atz ligand. Therefore, the magnetic data of **2** can be treated by a dinuclear model with a molecular field approximation to evaluate the inter-dinuclear interactions.^[23]

$$\chi_{\rm Mn_2^{\rm n}} = \frac{2Ng^2\beta^2}{kT} \times \frac{e^{2J/kT} + 5e^{6J/kT} + 14e^{12J/kT} + 30e^{20J/kT} + 55e^{30J/kT}}{1 + 3e^{2J/kT} + 5e^{6J/kT} + 7e^{12J/kT} + 9e^{20J/kT} + 11e^{30J/kT}}$$
(3)

$$\chi_{\rm M} T = \chi_{\rm Mn_2^{\pi}} T / [1 - (zJ'\chi_{\rm Mn_2^{\pi}} / Ng^2\beta^2)]$$
⁽⁴⁾

The best least-square fit of the theoretical Equation (3) and Equation (4) to the experimental magnetic data of **2** gave rise to g = 2.02, $J = -0.51 \text{ cm}^{-1}$, $zJ' = -0.15 \text{ cm}^{-1}$, and $R = 2.2 \times 10^{-4}$. The comparable values for J and zJ' reveal that the consistently antiferromagnetic interactions mediated by the triple heterobridges. It should be noted that the 2D {Mn(atz)} layer of **2** is structurally analogous to the {Cu₂(trz)₂} sheet of spin-canted [Cu^{II}₂Cu^I(trz)₃(Hbtc)]_n (trz = 1,2,4-triazolate, H₃btc = 1,3,5-benzenetricarboxylic acid).^[8] However, no spontaneous magnetization was found in **2** at low temperature. This is due to that the net magnetic generated by the dinuclear subunit is completely canceled out in the isotropic 2D magnetic layer of **2**.

The $\chi_{\rm M}T$ value of **3** is 4.49 cm³·K·mol⁻¹ at room temperature, which is close to the excepted value for one magnetically uncoupled Mn^{II} ion. Upon cooling, the $\chi_{\rm M}T$ product of **3** steadily decreases between 300 and 20 K and then abruptly down to 3.97 cm³·K·mol⁻¹ at 2.0 K. A plot of $\chi_{\rm M}^{-1}$ vs. *T* shows that **3** follows the Curie-Weiss law with C = 4.50 cm³·K·mol⁻¹ and $\theta = -0.40$ K. These features are indicative of weak antiferro-

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magnetic coupling between the discrete Mn^{II} units. The experimentally magnetic data of **3** can be analyzed by a mononuclear model with a molecular field approximation to evaluate the intermolecular interactions:^[23]

$$\chi = \frac{N\beta^2 g^2 S \left(S+1\right)}{3kT} \tag{5}$$

$$\chi_{\rm M} = \frac{\chi}{1 - (2zJ'/Ng^2 \beta^2)} \tag{6}$$

The least-squares fitting of magnetic susceptibilities data over the whole temperature range by Equation (5) and Equation (6) gives rise to g = 2.02, $zJ' = -0.03 \text{ cm}^{-1}$ and $R = 1.3 \times 10^{-4}$. The small negative coupling constant zJ' confirms the existence of rather weak antiferromagnetic exchange between the spin carriers through abundant hydrogen-bonding interactions. The magnetization of **3** increases quickly at low external magnetic elds below 30 kOe and slowly up to 5.03 $N\beta$ at 50 kOe (Figure 5b), corresponding to the saturation value (5.00 $N\beta$) for one Mn^{II} with paramagnetic S = 5/2 state.

Conclusions

Three 3-amino-1,2,4-triazole based magnetic samples consisting of two extended 3D frameworks and one discrete mononuclear molecule were obtained by incorporating with differently carboxylate-containing aromatic coligands. The combinatorial binding fashions of bi- and/or monodentate atz and carboxylate groups significantly determine the fundamental motifs and the dimensionality of the resulting complexes. Antiferromagnetic interactions with comparable coupling constants can be transmitted in the nearest spin carriers in the local Mn^{II} -COO⁻ chain of 1, in the Mn^{II} -atz-COO⁻ sublayer of 2, and by the hydrogen bonding of 3.

Experimental Section

Materials and General Methods: All chemicals were commercially purchased (3-amino-1,2,4-triazole, o-phthalic acid, 5-hydroxylisophthalic acid, and p-nitrobenzoic acid were from Acros; other analyticalgrade reagents were from Tianjin chemical reagent factory) and used as received without further purification. Elemental analyses for C, H, and N were carried out with a CE-440 (Leeman-Labs) analyzer. Fourier transform (FT) IR spectra (KBr pellets) were taken with an Avatar-370 (Nicolet) spectrometer in the range 4000-400 cm⁻¹. Thermogravimetric analysis (TGA) experiments were performed with a Shimadzu simultaneous DTG-60A compositional analysis instrument from room temperature to 800 °C in a nitrogen atmosphere at a heating rate of 5 K·min⁻¹. Powder X-ray diffraction (PXRD) patterns were obtained with a Bruker D8 ADVANCE diffractometer at 40 kV and 40 mA for Cu-K_a radiation ($\lambda = 1.5406$ Å), with a scan speed of 0.1 sec per step and a step size of 0.01° in 2θ . The simulated PXRD patterns were calculated using single-crystal X-ray diffraction data and processed by the free Mercury v1.4 program provided by the Cambridge Crystallographic Data Center. Magnetic susceptibilities were acquired with a Quantum Design SQUID MPMS-XL-7 magnetometer with polycrystalline samples, in which the phase purity of the samples was determined by PXRD experiments. The magnetic susceptibility was corrected for the contribution of the gel capsule and for the core diamagnetism (using Pascal's constants).

Synthesis of [Mn(atz)(pa)]_n (1): To an aqueous solution (4.0 mL) of Mn(NO₃)₂ (35.8 mg, 0.2 mmol) was slowly added a methanol solution (4.0 mL) containing H₂pa (16.6 mg, 0.1 mmol) and atz (25.2 mg, 0.3 mmol) with constant stirring. The pH value of the mixture was adjusted to 6 by triethylamine, and the resulting mixture was further stirred for 0.5 h and filtered. Upon slow evaporation of the solvent at room temperature, colorless block-shaped crystals of **1** were obtained within one month. Yield: 50.0% (based on H₂pa). $C_{30}H_{24}Mn_3N_{12}O_{12}$: calcd. C 39.62; H 2.66; N 18.48%; found C 39.63; H 2.63; N 18.49%. **IR** (KBr): $\tilde{v} = 3446$ (w), 3063 (w), 1654 (s), 1635 (s), 1559 (s), 1543 (s), 1505 (s), 1473 (m), 1406 (s), 1248 (w), 1081 (w), 770 (w), 694 (w), 665 (m), 647 (w), 615 (w), 549 (w) cm⁻¹.

Synthesis of {[Mn(atz)_{1.5}(hip)]·H₂O}_{*n*} (2): To a methanol solution (4.0 mL) containing atz (16.8 mg, 0.2 mmol) and H₂hip (18.2 mg, 0.1 mmol) was slowly added an aqueous solution (6.0 mL) of Mn(NO₃)₂ (26.8 mg, 0.15 mmol) with constant stirring. The resulting mixture was filtered after further stirring for 0.5 h. Colorless block-shaped crystals of **2** suitable for X-ray diffraction were generated by slow evaporation of the filtrate within two weeks. Yield: 66.7 % (based on H₂hip). C₁₁H₁₂MnN₆O₆: calcd. C 34.84; H 3.19; N 22.16 %; found C 34.85; H 3.21; N 22.18 %. **IR** (KBr): $\bar{v} = 3422$ (br), 1650 (s), 1557 (s), 1539 (s), 1508 (s), 1383 (s), 1272 (w), 961 (w), 792 (w), 671 (m), 547 (w), 453 (w) cm⁻¹.

Synthesis of $[Mn(H_2O)_2(atz)_2(nb)_2]$ (3): To an aqueous solution (6.0 mL) of $Mn(ClO_4)_2$ ·6H₂O (72.4 mg, 0.2 mmol) was slowly added a methanol solution (4.0 mL) containing Hnb (16.7 mg, 0.1 mmol) and atz (25.2 mg, 0.3 mmol) with constant stirring. The pH value of the mixture was adjusted to 6 by triethylamine, and the resulting mixture was filtered by further stirring for 0.5 h. Upon slow evaporation of the solvent at room temperature, colorless block-shaped crystals of **3** were obtained within one month. Yield: 25.0% (based on Hnb). $C_{18}H_{20}MnN_{10}O_{10}$: calcd. C 36.56; H 3.41; N 23.69%; found C 36.55; H 3.43; N 23.66%. **IR** (KBr): $\tilde{v} = 3462$ (w), 3366 (s), 3069 (w), 1613 (s), 1578 (s), 1556 (s), 1515 (s), 1382 (s), 1343 (s), 1318 (m), 1261 (m), 1065 (m), 798 (m), 723 (s), 704 (w), 523 (m) cm⁻¹.

X-ray Data Collection and Structure Determinations: Diffraction intensities for 1-3 were collected with a Bruker APEX-II QUAZAR diffractometer equipped with graphite-monochromated Mo- K_{α} radiation with a radiation wavelength of 0.71073 Å by using the ϕ - ω scan technique at 173(2) K. Semiempirical multi-scan absorption corrections were applied by SADABS, and the program SAINT was used for integration of the diffraction profiles.^[26] The structures were solved by direct methods and refined with the full-matrix least-squares technique using the SHELXS-97 and SHELXL-97 programs.^[27] Non-hydrogen atoms were located by difference Fourier maps and subjected to anisotropic refinement. The hydrogen atom was added according to theoretical models. The oxygen atom of the lattice water molecule (O6) in 2 was varied between two positions with the site occupancies of 0.78 for O6 and 0.22 for O6'. No hydrogen atoms were located for the disordered water molecule. Detailed crystallographic data are summarized in Table 1. Selected bond lengths and angles are given in Table 2, Table 3, and Table 4, respectively.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-910490, CCDC-910491, and CCDC-910492 (for complexes **1–3**) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

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Supporting Information (see footnote on the first page of this article): Hydrogen-bonding parameters for **3** and PXRD patterns for **1–3**.

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References

- [1] O. Kahn, C. J. Martinez, Science 1998, 279, 44.
- [2] X.-Y. Wang, Z.-M. Wang, S. Gao, Chem. Commun. 2008, 281.
- [3] a) Y.-F. Zeng, X. Hu, F.-C. Liu, X.-H. Bu, *Chem. Soc. Rev.* 2009, 38, 469; b) J.-R. Li, Q. Yu, E. C. Sañudo, Y. Tao, X.-H. Bu, *Chem. Commun.* 2007, 2602.
- [4] a) W. Ouellette, M.-H. Yu, C. J. O'Connor, D. Hagrman, J. Zubieta, *Angew. Chem. Int. Ed.* 2006, 45, 3497; b) W. Ouellette, J. R. Galan-Mascaros, K. R. Dunbar, J. Zubieta, *Inorg. Chem.* 2006, 45, 1909; c) P. J. Hagrman, C. Bridges, J. E. Greedan, J. Zubieta, *J. Chem. Soc. Dalton Trans.* 1999, 2901; d) W. Ouellette, S. Jones, J. Zubieta, *CrystEngComm* 2011, 13, 4457; e) W. Ouellette, A. V. Prosvirin, J. Valeich, K. R. Dunbar, J. Zubieta, *Inorg. Chem.* 2007, 46, 9067.
- [5] Y. Li, W.-Q. Zou, M.-F. Wu, J.-D. Lin, F.-K. Zheng, Z.-F. Liu, S.-H. Wang, G.-C. Guo, J.-S. Huang, *CrystEngComm* 2011, 13, 3868.
- [6] a) J.-P. Zhang, Y.-B. Zhang, J.-B. Lin, X.-M. Chen, *Chem. Rev.* **2012**, *112*, 1001; b) W.-X. Zhang, X. Wei, Y.-Z. Zheng, X.-M. Chen, *Chem. Commun.* **2009**, 3804.
- [7] a) E.-C. Yang, Z.-Y. Liu, L.-N. Zhao, X.-J. Zhao, *CrystEngComm* 2011, 13, 5401; b) E.-C. Yang, Y.-L. Yang, Z.-Y. Liu, K.-S. Liu, X.-Y. Wu, X.-J. Zhao, *CrystEngComm* 2011, 13, 2667; c) E.-C. Yang, B. Ding, Z.-Y. Liu, Y.-L. Yang, X.-J. Zhao, *Cryst. Growth Des.* 2012, 12, 1185; d) E.-C. Yang, Z.-Y. Liu, T.-Y. Liu, L.-L. Li, X.-J. Zhao, *Dalton Trans.* 2011, 40, 8132; e) Z.-Y. Liu, B. Ding, E.-C. Yang, X.-J. Zhao, *Dalton Trans.* 2012, 41, 9611; f) E.-C. Yang, Z.-Y. Liu, Y.-L. Yang, J.-Y. Wang, X.-J. Zhao, *Dalton Trans.* 2011, 40, 8513.
- [8] E.-C. Yang, Z.-Y. Liu, X.-J. Shi, Q.-Q. Liang, X.-J. Zhao, *Inorg. Chem.* 2010, 49, 7969.
- [9] M. H. Klingele, P. D. W. Boyd, B. Moubaraki, K. S. Murray, S. Brooker, *Eur. J. Inorg. Chem.* 2005, 910.

- [10] S. Ferrer, P. J. van Korringsbruggen, J. G. Haasnoot, J. Reedijk, H. Kooijman, A. L. Spek, L. Lezama, A. M. Arif, J. S. Miller, J. Chem. Soc. Dalton Trans. 1999, 4269.
- [11] D. Sarma, V. Srivastava, S. Natarajan, *Dalton Trans.* 2012, 41, 4135.
- [12] S.-P. Chen, S. Shu, S.-L. Gao, Inorg. Chim. Acta 2009, 362, 3043.
- [13] a) Z.-G. Gu, Y.-F. Xu, X.-H. Zhou, J.-L. Zuo, X.-Z. You, *Cryst. Growth Des.* **2008**, *8*, 1306; b) J.-C. Liu, G.-C. Guo, J.-S. Huang, X.-Z. You, *Inorg. Chem.* **2003**, *42*, 235; c) J.-H. Zhou, R.-M. Cheng, Y. Song, Y.-Z. Li, Z. Yu, X.-T. Chen, Z.-L. Xue, X.-Z. You, *Inorg. Chem.* **2005**, *44*, 8011.
- [14] B. Liu, Y.-H. Chen, X.-C. Zhang, Inorg. Chem. Commun. 2008, 11, 965.
- [15] B. Ding, Y.-Q. Huang, Y.-Y. Liu, W. Shi, P. Cheng, *Inorg. Chem. Commun.* 2007, 10, 7.
- [16] a) Q.Q. Liang, Z.Y. Liu, E.C. Yang, X.J. Zhao, Z. Anorg. Allg. Chem. 2009, 635, 2653; b) E.-C. Yang, Z.-Y. Liu, X.-Y. Wu, H. Chang, E.-C. Wang, X.-J. Zhao, Dalton Trans. 2011, 40, 10082.
- [17] E.-C. Yang, Z.-Y. Liu, C.-H. Zhang, Y.-L. Yang, X.-J. Zhao, *Dal-ton Trans.* 2013, 42, 1581.
- [18] M. Tabatabaee, B.-M. Kukovec, M. Kazeroonizadeh, *Polyhedron* **2011**, *30*, 1114.
- [19] P.-X. Yin, Z.-J. Li, J. Zhang, L. Zhang, Q.-P. Lin, Y.-Y. Qin, Y.-G. Yao, *CrystEngComm* **2009**, *11*, 2734.
- [20] a) P. Kar, Y. Ida, T. Ishida, A. Ghosh, *CrystEngComm* 2013, 15, 400; b) P. Kar, R. Biswas, Y. Ida, T. Ishida, A. Ghosh, *Cryst. Growth Des.* 2011, 11, 5305.
- [21] K. Nakamoto, Infrared and Roman Spectra of Inorganic and Coordination Compounds, Wiley, New York, **1986**.
- [22] A. L. Spek, *PLATON*, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, 2001.
- [23] O. Kahn, *Molecular Magnetism*, VCH, Weinheim, Germany, 1993.
- [24] C.-B. Ma, W.-G. Wang, X.-F. Zhang, C.-N. Chen, Q.-T. Liu, H.-P. Zhu, D.-Z. Liao, L.-C. Li, *Eur. J. Inorg. Chem.* 2004, 3522.
- [25] G. Fernandez, M. Corbella, J. Mahia, M. A. Maestro, Eur. J. Inorg. Chem. 2002, 2502.
- [26] Bruker AXS, SAINT Software Reference Manual, Madison, WI, 1998.
- [27] a) G. M. Sheldrick, SHELXL-97 Program for X-ray Crystal Structure Refinement, Göttingen University, Göttingen, Germany, 1997; b) G. M. Sheldrick, SHELXS-97 Program for X-ray Crystal Structure Solution, Göttingen University, Göttingen, Germany, 1997.

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