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3D azido-bridged cobalt(II) complexes with diazines as coligands

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1. Introduction

In recent years a great number of 1D to 3D polynuclear derivatives from paramagnetic 3d ions have been prepared with the aim to obtain molecular magnets with high critical temperatures. From the synthetic point of view these polynuclear compounds have been usually built by mixing the paramagnetic spin carriers with suitable bridging and terminal ligands. Between the potential 3d spin carriers the Mn(II) has been extensively employed combined with three-atom azido bridging ligand. With the above mentioned strategy, a great number of compounds with general formula [Mn(N₃)₂(L)₂] have been reported. L are usually R-pyridine monodentate ligands or (L)₂ one bidentate aromatic N-donor ligand. These compounds show all range of dimensionalities: from cluster to 3D systems [1-13]. The azido bridging ligand shows also the capability to coordinate in different modes, mainly in the $\mu_{1,3}$ (end-to-end, EE) or $\mu_{1,1}$ (end-on, EO) modes, which can be present simultaneously in the same $[Mn(N_3)_2(L)_2]$ compound. The different dimensionalities plus the different coordination modes generate a great number of topologies. Taking into account that the EE coordination mode typically promotes antiferromagnetic, AF, interactions and the EO coordination mode promotes ferromagnetic, F, interactions, the great diversity of dimensionalities and topologies found in the $[Mn(N_3)_2(L)_2]$ compounds has as consequence a great diversity in their magnetic behavior.

Focusing our attention on the synthesis of 3D compounds, one synthetic strategy is based in mixing Mn(II) salts with the azido

ABSTRACT

Two new three-dimensional azido-bridged Co(II) compounds with formula $[Co(N_3)_2(2,5-Me_2pyz)]_n$ (1) and $[Co(N_3)_2(2-ampym)]_n$ (2) have been structurally and magnetically characterized. 2,5-Me_2pyz and 2-ampym are 2,5-dimethylpyrazine and 2-aminopyrimidine, respectively. Compound 1 crystallizes in the monoclinic system with space group $P2_1/c$ and compound 2 in the orthorhombic system with space group $P2_1/c$ and compound 2 in the orthorhombic system with space group P1ma. In 1 and 2 each cobalt atom is linked to the four nearest-neighbors by end-to-end (EE) azido bridges, forming square layers. These layers are further connected to 3D networks by the N,N'-bridging ligands 2,5-dimethylpyrazine or 2-aminopyrimidine. The magnetic properties of 1 and 2 are reported. The plots of χ_M or $\chi_M T$ for 1 and 2 show antiferromagnetic coupling.

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and other potentially bridging ligands as 1,3- or 1,4-diazines [14,15]. Taking into account other spin carriers like Co(II), the reported 1D to 3D [Co(N₃)₂(L)₂] compounds are scarce [15–32], although the number has quickly increased mainly after the publication of the double end-on (EO) azido bridged single-chain magnet (SCM) [Co(2,2'-bithiazoline)(N₃)₂] [18]. The low number of fully characterized [Co(N₃)₂(L)₂] compounds is not surprising due to synthetic problems: in the case of the Mn(II) derivatives, by slow evaporation of methanol or water/methanol solutions of Mn(II) salts, R-pyridine monodentate or bidentate aromatic N-donor ligands and sodium azide, it is possible to obtain well formed single crystals suitable for X-ray structural determination. In case of the Co(II) salts, the same procedure usually generates a microcrystalline precipitate in few seconds.

The combination of the anisotropic Co(II) cation with the coordination versatility and the consequent different superexchange coupling pathways of the azido bridging ligand, has produced several interesting compounds from the magnetic and structural points of view like the compound $[Co(N_3)_2(bpg)](DMF)_{4/3}$ (bpg = meso- α,β -bi(4-pyridyl)glycol) showing a Kagomé layer [19] or the weak ferromagnet $[Co(\mu_{1,3}-N_3)_2(4-acpy)_2]_n$ (4-acpy = 4-acetyl-pyridine) [24,25]. A unique 3D Co(II)-azido sublattice has been found in the ferromagnet $[Co_2(N_3)_4(hmt)(H_2O)]_n$ (hmt = hexameth-ylenetetramine) [28]. Very recently, new 1D systems exhibiting ferrimagnetic [29] or single-chain magnetic behavior [30,31] have been described.

In this paper, we report two new three-dimensional azidobridged Co(II) compounds with formula $[Co(N_3)_2(2,5-Me_2pyz)]_n$ (1) and $[Co(N_3)_2(2-ampym)]_n$ (2), 2,5-Me₂pyz and 2-ampym are 2,5-dimethylpyrazine and 2-aminopyrimidine, respectively, which



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are built from the above described strategy to mix Co(II) salts, azido ligand and other potentially bridging ligands as 1,3- or 1,4-diazines, along with their magnetic properties.

2. Experimental

2.1. General

Cobalt(II) chloride hexahydrate, sodium azide, 2-aminopyrimidine and 2,5-dimethylpyrazine (Aldrich) were used as obtained. Aqueous hydrazoic acid is obtained with a modified Kipp's generator by decomposition of NaN₃ in H₂SO₄/H₂O (1:3 v:v) and subsequent transfer of HN₃ into H₂O with aid of an inert-gas stream [33]. Diluted HN₃ in the synthesis of the complexes is used to avoid anionic impurities, like OH⁻ (hydrolysis) or CO₃²⁻ (CO₂ uptake from air).

Caution! Azide compounds and hydrazoic acid (HN_3) are potentially explosive! Only small amount of material should be prepared, and it should be handled with care.

2.2. $[Co(N_3)_2(2,5-Me_2pyz)]_n$ (1)

CoCl₂·6H₂O (0.480 g, 2.02 mmol), 2,5-dimethylpyrazine (0.220 g, 2.03 mmol), and NaN₃ (0.293 g, 4.50 mmol) were dissolved in 5.00 mL aqueous hydrazoic acid at room temperature. After 3 days dark red crystals of **1** were separated. Yield: 0.146 g (28.6%). Calc. for C₆H₈CoN₈ (251.13): C, 28.7; H, 3.2; Co, 23.5; N, 44.6. Found: C, 28.6; H, 3.3; Co, 23.7; N, 44.4%. IR (KBr, cm⁻¹) 3409 (w), 2079 (vs) v_{as} (N₃), 1494 (m), 1451 (m), 1381 (w), 1326 (m), 1156 (m), 1071 (m), 1032 (w), 979 (w), 895 (w), 467 (m).

2.3. $[Co(N_3)_2(2-ampym)]_n$ (2)

CoCl₂·6H₂O (0.490 g, 2.07 mmol), 2-aminopyrimidine (0.270 g, 2.82 mmol), and NaN₃ (0.293 g, 4.50 mmol) were dissolved in 26.0 mL aqueous hydrazoic acid by heating up to 90 °C. Upon slow cooling to 4 °C red crystals of **2** were separated after one week. Yield: 0.375 g (77.2%). Calc. for C₄H₅CoN₉ (238.10): C, 20.2; H, 2.1; Co, 24.8; N, 52.9. Found: C, 20.0; H, 1.9; Co, 24.9; N, 53.2%. IR (KBr, cm⁻¹) 3471 (m), 3418 (w), 3372 (m), 2082 (vs) ν_{as} (N₃), 1637 (s), 1579 (s), 1487 (s), 1461 (m), 1357 (m), 1241 (w), 1201 (m), 1101 (w), 995 (w), 791 (m), 662 (w), 637 (w), 615 (w), 532 (w), 475 (m).

2.4. Spectral and magnetic measurements

Infrared spectra were recorded (4000–400 cm⁻¹) with a Perkin– Elmer 1600 Series FT-IR spectrophotometer as KBr pellets. Magnetic susceptibility measurements under several magnetic fields in the temperature range 2–300 K and magnetization measurements in the field range of 0–5 T were performed with a Quantum Design MPMS-XL SQUID magnetometer at the Magnetochemistry Service of the University of Barcelona. All measurements were performed on polycrystalline samples. Pascal's constants were used to estimate the diamagnetic corrections, which were subtracted from the experimental susceptibilities to give the corrected molar magnetic susceptibilities.

2.5. X-ray crystallography

The single-crystal diffraction studies of both complexes were performed with a Bruker APEX II CCD diffractometer equipped with graphite-monochromated Mo K α radiation (λ = 0.71073 Å) by using the ω -scan technique at 100(2) K. The SMART and SAINT software packages [34] were used for data collection and integration,

respectively. Crystallographic data and some features of the structure refinements are summarized in Table 1. The collected data were corrected for absorption by using sADABS [35] based upon Laue symmetry by using equivalent reflections. The structures were solved by direct methods and refined with the full-matrix leastsquares technique by using the SHELXTL/PC program package [36]. All non-hydrogen atoms were refined anisotropically, whereas all the H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms.

3. Results and discussion

3.1. Crystal structures

3.1.1. Description of the structure of $[Co(N_3)_2(2,5-Me_2pyz)]_n$ (1)

The three-dimensional neutral cobalt-azido compound 1 can be described as square layers with only EE azido bridges. N,N'-bridging 2,5-dimethylpyrazine ligands further connect the 2D Co-azidosublattice to form a 3D network structure. A perspective view of 1 together with the atom numbering scheme is presented in Fig. 1a. The Co(1) is located at center of inversion and is coordinated by six nitrogen atoms with a slightly elongated octahedral geometry. Two N atoms in trans-position are part of two 2,5-dimethylpyrazine ligands. The remaining equatorial N atoms belong to four azido groups linked to four different cobalt atoms in an EE bridging mode generating two-dimensional Co(N₃)₂ layers extended parallel to the *bc*-plane of the monoclinic unit cell (Fig. 1b and c). The Co-N(azido) bond distances are 2.108(2) and 2.141(2) Å, whereas the Co-N(2,5-Me₂pyz) is 2.224(2) Å. The Co(1)-N(11)-N(12), Co(1)-N(13)-N(12C) and N(11)-N(12)-N(13F) bond angles are 139.6(2)°, 122.7(2)° and 177.9(3)°, respectively. The Co-NNN-Co' torsion angles are $\pm 100.2(4)^{\circ}$ and the dihedral angle between $\mu_{1,3}$ -N₃-bridged CoN₄(azido)-planes is 13.4°. The Co azido layers are further linked along the *a*-axis by the ring N atoms of the 2,5-dimethylpyrazine ligands thus forming the 3D network. The $Co(1) \cdots Co(1C)$ intralayer distance is 5.6932(13) Å. The Co(1) $\cdot \cdot \cdot$ Co(1A) interlayer separation is 7.2360(16) Å.

3.1.2. Description of the structure of $[Co(N_3)_2(2-ampym)]_n$ (2)

Complex **2** crystallizes in space group *Pnma* of the orthorhombic crystal system. The atom numbering scheme is presented in Fig. 2a. As in complex **1**, a three-dimensional neutral 3D network is formed

Table 1Crystal data and structure refinement for compounds 1 and 2.

Compound	1	2
Empirical formula	C ₆ H ₈ CoN ₈	C ₄ H ₅ CoN ₉
Formula weight	251.13	238.10
T (K)	100(2)	100(2)
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/c$	Pnma
a (Å)	7.2360(14)	7.0878(14)
b (Å)	6.9775(14)	12.883(3)
c (Å)	8.998(2)	8.905(2)
β (°)	107.52(3)	90
V (Å ³)	433.2(2)	813.1(3)
Ζ	2	4
F(0 0 0)	254	476
Crystal size (mm)	$0.30 \times 0.20 \times 0.10$	$0.30 \times 0.22 \times 0.15$
D_{calc} (g cm ⁻³)	1.925	1.945
μ (Mo K $lpha$) (mm $^{-1}$)	1.958	2.084
Collected data	2888	5956
Independent reflections (R _{int})	880 (0.0324)	860 (0.0259)
Parameters	71	74
$R_1 \left[I > 2\sigma(I) \right]$	0.0345	0.0269
wR_2 (all data)	0.0815	0.0632
Goodness-of-fit (GOF) on F^2	1.092	1.206
Residual extrema (e Å ⁻³)	0.463/-0.467	0.276/-0.311



Fig. 1. (a) Perspective view of **1** showing the atom-numbering scheme. Ellipsoid are at the 50% propability level. Symmetry codes: (A) -x + 2, -y + 2, -z; (B) -x + 1, -y + 2, -z; (C) -x + 1, y + 1/2, -z + 1/2; (D) x, -y + 3/2, z - 1/2; (E) x, -y + 5/2, z - 1/2; (F) -x + 1, y - 1/2, -z + 1/2. (b) Packing view of **1** along [0 1 0]. (c) Packing view of **1** along [1 0 0].

by connecting square layers with only EE azido bridges via N.N'bridging 2-aminopyrimidine ligands. Each Co(II) metal ion, located at a center of inversion, is coordinated octahedrally by six N atoms of which two are part of the 2-aminopyrimidine ligands and the other four belong to azide groups. The Co-N(azido) bond lengths are 2.120(2) and 2.128(2) Å, whereas the axial Co-N(2-ampym) is 2.200(2) Å. The Co(1)-N(11)-N(12), Co(1)-N(13)-N(12B) and N(11)-N(12)-N(13C) bond angles are 121.48(12)°, 132.06(12)° and 177.9(2)°, respectively. The Co-NNN-Co' torsion angles are $\pm 116.4(2)^{\circ}$. The dihedral angle between $\mu_{1,3}$ -N₃-bridged CoN₄(azido)-planes within the Co-azide layer is 18.2°, whereas the dihedral angle between CoN₄(azido)-planes of Co(1) and Co(1D) is 45.9°. The Co azido layers are further linked along the *b*-axis by the ring N atoms of the 2-aminopyrimidine ligands thus forming the 3D network (Fig. 2b and c). The $Co(1) \cdots Co(1C)$ intralayer distance is 5.6907(13) Å. The Co(1) \cdots Co(1A) interlayer separation is 6.4415 (15) Å. The aromatic rings of the 2-aminopyrimidine molecules form dihedral angles of 42.3°, in contrast to $[Co(N_3)_2(pym)]_n$ [15], where the pyrimidine rings have a coplanar arrangement. The amino groups form hydrogen bonds of type N-H...N to azide nitrogen atoms $[N(2) \cdots N(11) = 3.018(2) \text{ Å}$, and N(2)-N(13) = 3.091(2) Å].

3.2. Magnetic properties

The magnetic properties of **1** and **2**, in the form of $\chi_{\rm M}$ versus *T* are presented for the value of the applied magnetic field of 5000 G (Fig. 3). The room temperature $\chi_{\rm M}$ values of 9.17×10^{-3} and 9.32×10^{-3} cm³ mol⁻¹ for **1** and **2**, respectively increase upon lowering the temperature in a similar manner, reaching sharp maxima of 45×10^{-3} cm³ mol⁻¹ at 20 K for **1** and of 27×10^{-3} cm³ mol⁻¹ at 45 K for **2**. After the maxima, the $\chi_{\rm M}$ values decrease quickly, to ar-

rive at minimum values of $28 \times 10^{-3} \text{ cm}^3 \text{ mol}^{-1}$ at 8 K for 1 and $16\times10^{-3}~cm^3~mol^{-1}$ at 12 K for **2**. At 2 K the χ_M values are 30×10^{-3} and $17\times10^{-3}~cm^3~mol^{-1}$ for **1** and **2**, respectively. The sharp maxima in the $\gamma_{\rm M}$ versus T plots for **1** and **2** can indicate 3D antiferromagnetic ordering below the temperature of these maxima. For **1** and **2** the $\gamma_{M}T$ room temperature values decrease continuously upon lowering the temperature with a change of slope around 20 K for 1 and 45 K for 2, Fig. 4. The magnetic susceptibility in the range 30-300 K for 1 and 50-300 K for 2 obeys the Curie–Weiss law ($\chi_{\rm M} = C/(T - \theta)$) with C = 3.35 and $\theta = -69.3$ K for **1** and C = 3.63 and $\theta = -86.7$ K for **2**. The C values of 3.35 and 3.63 correspond to g values of 2.67 and 2.78 for 1 and 2, respectively. The negative Weiss constants for **1** and **2** in the respective high temperature ranges indicate antiferromagnetic coupling in both compounds between Co(II) ions bridged by EE azido and N,N'-diazine ligands. The Néel temperature, $T_{\rm N}$, for complexes **1** and **2** was determined by the in phase of zero field ac magnetic susceptibility $\chi'(T)$ which has maxima of 19.5 and 42.5 K for **1** and **2**, respectively under H_{ac} = 4 Oe and frequency of 957 Hz. For 1, the magnetization at 2 K increases upon increasing the applied field with a change of slope around 2.5 T to a value of 0.33 N β at 5 T, far from the saturation value of the Co^{2+} ion, which suggest a strong 3D antiferromagnetic ordering. For 2, the magnetization at 2 K increases upon increasing the applied field to a value of 0.13 Nβ at 5 T without change of slope, far also from the saturation value of the Co²⁺ ion suggesting also a strong 3D antiferromagnetic ordering.

In Table 2 are shown some structural and magnetic data for the reported 2D or 3D azido–Co(II) compounds built from 2D (4,4) Co($\mu_{1,3}$ -N₃)₂ layers. The compounds **1–4** order antiferromagnetically below *T*_N in the range 7.8–42 K whereas the compounds **5–**



Fig. 2. (a) Perspective view of **2** showing the atom-numbering scheme. Ellipsoid are at the 50% propability level. Symmetry codes: (A) -x, -y + 1, -z; (B) -x - 1/2, -y + 1, z - 1/2; (C) -x - 1/2, -y + 1, z + 1/2; (D) x, -y + 3/2, z. (b) Packing view of **2** along [1 0 0]. (c) Packing view of **2** along [0 1 0].



Fig. 3. Plot of χ_M vs. *T* in the 300–2 K range of temperature for $[Co(N_3)_2(2,5-Me_2pyz)]_n$ (1) (open dots) and $[Co(N_3)_2(2-ampym)]_n$ (2) (black dots) measured under external magnetic field of 5000 G. The solid line shows the best fit in the high-temperature region as Curie–Weiss law (see text).

8 are weak ferromagnets below $T_{\rm C}$ in the range 10–23 K. Taking into account the (CH₂)₄ linker in the formally 3D compound **7**, **5**–**8** can be considered from the magnetic point of view as spincanted layers ferromagnetically ordered below $T_{\rm C}$ through dipolar interactions [26]. The Co···Co interlayer distances in **5–8** are in the range 10.6–15.2 Å. For compounds **1–3** the 3D AF ordering below $T_{\rm N}$ in the range 19.5–42.5 K can be explained from the AF cou-



Fig. 4. Plot of $\chi_M T$ vs. *T* in the 300–2 K range of temperature for $[Co(N_3)_2(2,5-Me_2pyz)]_n$ (1) (open dots) and $[Co(N_3)_2(2-ampym)]_n$ (2) (black dots) measured under external magnetic field of 5000 G.

pling between the 2D (4,4) $Co(\mu_{1,3}-N_3)_2$ layers through the N,N'diazine bridging ligands. In compound **4** the 2D (4,4) $Co(\mu_{1,3}-N_3)_2$ layers are bridged through the 1,4-bis(tetrazole-1-yl)ethane (endi) ligand. In this case the 3D AF ordering below $T_N = 7.8$ K is more difficult to explain because the endi ligand is a $(CH_2)_2$ linker. Gao et al. explain the absence of the spin canting in **4** for its unique triclinic crystal system [26]. The Co···Co interlayer distances in **1–4** are in the range 6.0–8.7 Å.

Table 2	
Some structural and magnetic data for compounds with Co(II) azide (4,4) square lay	vers.

Compound ^a	1	2	3	4	5	6	7	8
Dimension	3D	3D	3D	3D	2D	2D	3D	2D
Co–N _L (Å) ^b	2.224	2.200	2.165	2.144, 2.125	2.172	2.185	2.127	2.136, 2.139
$Co-N(N_3)$ (Å)	2.108	2.120	2.123	2.140, 2.118	2.125	2.113	2.100	2.099, 2.103
	2.141	2.128	2.125	2.136, 2.095	2.133	2.142	2.158	2.161, 2.158
Co-N-N (°)	139.6	132.1	125.6	123.6, 136.7	149.2	150.0	145.7	146.1, 146.2
	122.7	121.5	124.1	140.1, 145.1	128.2	121.1	119.0	120.1, 120.3
Co···Co (Å) (intra-layer)	5.6932	5.6907	5.739, 5.599	5.746	5.848	5.932	5.794	5.845, 5.842
Co…Co (Å) (inter-layer)	7.2360	6.4415	5.978	8.68	11.73	13.60	10.633	15.18, 15.172
$\tau_{\text{Co-N-N-Co}}(\circ)$	100.2	116.4	108.5, 133.4	107.9, 75.2	84.9	131.0	122.5	124.1, 123.7
δ (°) ^c	13.4	18.2	68.8	81.7	83.3	55.5	62.1	61.1, 61.2
N_L –Co···Co– N_L (°)	5.7	8.9	55.2/50.0	75.0	62.3	50.0	-	58.9
$T_{\rm C}$ or $T_{\rm N}$ (K)	$T_{\rm N} = 19.5$	$T_{\rm N} = 42.5$	$T_{\rm N} = 41$	$T_{\rm N} = 7.8$	$T_{\rm C} = 11.2$	$T_{\rm C} = 10$	$T_{\rm C} = 23$	$T_{\rm C} = 22.1$
Magn. behavior below $T_{\rm C}$ or $T_{\rm N}$	AF	AF	AF	AF	weak F	weak F	weak F	weak F
$C (\text{cm}^3 \text{ mol}^{-1} \text{ K})/\theta (\text{K})^{\text{d}}$	3.35/-69.3	3.63/-86.7	3.38/-104	3.62/-48.5	3.55/-45.4	3.25/-54.1	3.36/-59.3	3.04 (3.40)/-48.2 (-54.2)
Reference	this work	this work	[15]	[26]	[24,25]	[19]	[27]	[26,27]

^a Compound **3**: $[Co(N_3)_2(pym)]_n$ (pym = pyrimidine); compound **4**: $[Co(N_3)_2(endi)]_n$ (endi = 1,2-(tetrazole-1-yl)ethane); compound **5**: $[Co(N_3)_2(4-acpy)]_n$ (4-acpy = 4-ace-tylpyridine); compound **6**: $[Co(N_3)_2(bpg)]_n$ (bgp = meso- α,β -bi(4-pyridyl)glycol); compound **7**: $[Co(N_3)_2(btzb)]_n$ (btzb = 1,4-(tetrazole-1-yl)butane); compound **8**: $[Co(N_3)_2(btze)]_n$ (btzb = 1,4-(tetrazole-1-yl)butane); compound **8**: [Co

^b N_L coordinated N atom of organic ligand L.

^c Dihedral angle between neighboring [CoN₄] planes defined by azido N atoms.

^d Corresponding parameters from Curie–Weiss law ($\chi_M = C/(T - \theta)$).

4. Conclusion

Here we have presented two new 3D azido–Co(II) compounds and similar structural motif: $Co(\mu_{1,3}-N_3)_2$ square layers connected via N,N'-diazine ligands: $[Co(N_3)_2(Me_2pyz)]_n$ (1) and $[Co(N_3)_2(2-ampym)]_n$ (2). Compounds 1 and 2 show 3D antiferromagnetic coupling below T_N = 19.5 and 42.5 K, respectively. From the point of view of possible useful magnetic properties to be applied in devices, it is important to have high T_c values in compounds built from M($\mu_{1,3}$ -N₃)₂ square layers. For this reason the synthetic strategy to bind antiferromagnetically the spin canted 2D M($\mu_{1,3}$ -N₃)₂ planes through N,N'-diazine ligands should be avoided.

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Appendix A. Supplementary material

Selected bond parameters for **1** (Table S1) and **2** (Table S2). AC susceptibility data of **1** (Figure S1) and of **2** (Figure S2) at an ac magnetic field of 4 Oe with a frequency of 957 Hz. CCDC 714909 and 714910 contain the supplementary crystallographic data for **1** and **2**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.bbrc.2005. 06.209.

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