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Synthesis and Characterization of a Ladder-Like Coordination Polymer Composed of Trimanganese Clusters Formed and Linked by Isophthalato Ligands

Cheng-Bing Ma,[a] Chang-Neng Chen,[a] Qiu-Tian Liu,*[a] Dai-Zheng Liao,[b] and Li-Cun Li[b]

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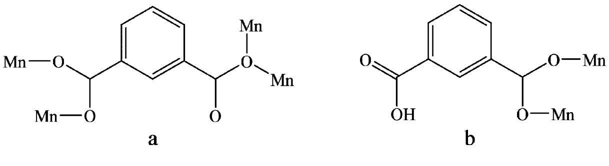
A new isophthalatomanganese(II) coordination polymer, $[Mn_3(ip)_2(Hip)_2(bipy)_2]_n{\cdot}2.5nH_2O$ [H_2ip = isophthalic acid, bipy = 2,2′-bipyridine], has been obtained directly by heating to reflux a weakly acidic solution containing bipy, $Mn(OAc)_2{\cdot}4H_2O$, and H_2ip. The polymer was characterized by single-crystal X-ray diffraction and magnetic measurements. The complex contains rare isophthalato-bridged trimanganese cluster building units further linked by isophthalato ligands in a newly observed binding mode, forming a one-dimensional, ladder-like chain network. The magnetic interactions within the complex were quantitatively evaluated by using a combination of a trimeric model and a mean molecular field approximation model. The complex was shown to be antiferromagnetic like other discrete trimanganese clusters with a structurally similar core.

Introduction

Metal–organic hybrid extended solids, mostly constructed from mononuclear metal centers and organic ligands, have been extensively studied in the past few decades, because of their fascinating network topologies and crystal packing motifs[1] as well as their promising applications as functional materials.[2] Less attention has been paid to the use of multimetallic clusters as building units for the synthesis of these polymeric materials, though it is easily understood that the metallic clusters may introduce their inherent extraordinary physical properties to the polymeric frameworks,[3,4] and that usually the exceptional stability of polymerized products makes them more promising in potential applications than the metallic clusters themselves.[5] The key to constructing such frameworks is the selection of stable metallic cluster building blocks, which resist decomposition during the polymerization reaction, and multidentate organic ligands, which are not only suitable for bridging and/or forming metallic clusters but are also inactive in inducing the transformation of the metallic cluster into a common structure with the single-metal centers as building blocks.

The magnetic properties of the trinuclear clusters of the type $[Mn_3(RCOO)_6(L)_2]$, exhibiting spin crossover at high magnetic field, have been well documented.[6] A suitable modification of the R group attached to the carboxylate function would be expected to induce aggregates of the trimeric units. Isophthalic acid has shown versatile binding ability, as manifested by the formation of one- and two-dimensional polymeric manganese(II) complexes with either mononuclear or dinuclear metal centers in repeating units.[7] In view of the fact that its two carboxyl groups are separated by a long distance, isophthalic acid would also be anticipated to form, as benzoic acid does, a $[Mn_3(RCOO)_6(L)_2]$ unit through one of carboxyl groups and to further link together these units to afford a polymeric structure through the other.

Herein, we report a novel ladder-like coordination polymer consisting of linear isophthalato-bridged trimanganese(II) cluster units held together by the isophthalato ligands in a newly observed binding mode (Scheme 1a), $[Mn_3(ip)_2(Hip)_2(bipy)_2]_n{\cdot}2.5nH_2O$. The complex has magnetic behavior resembling that of discrete carboxylatotrimanganese(II) complexes featuring a similar core structure.



Scheme 1. Binding modes of the isophthalato ligand found in this work.

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[a] State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences
Fuzhou, Fujian 350002, P. R. China
Fax: + 86-591-83792395
E-mail: lqt@fjirsm.ac.cn
[b] Department of Chemistry, Nankai University
Tianjin 300071, P. R. China

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Results and Discussion

Synthesis, IR Spectroscopy, TGA and X-ray Powder Diffraction Studies

In the reaction of isophthalic acid with a Mn^{2+} salt, weakly acidic conditions are adopted to avoid rapid polymerization favoring the formation of insoluble polymeric precipitates, as it is known that an acidic medium can decrease the concentration of the ip dianion formed as a result of the deprotonation process: $H_2ip \rightleftharpoons H^+ + Hip^- \rightleftharpoons 2H^+ + ip^{2-}$. The isolation of a complex with novel trimetallic-cluster-based ladder-like structure instead of the extensively reported common chain type[7a] indicates that maintaining the appropriate acidity may play an important role in the formation of this specific structure. Direct deposition of single crystals of the complex from a solution heated to reflux in an open system is fairly appealing, though the mechanism remains unclear, and the controllable conditions should be further optimized.

The IR spectrum offers some valuable information on both the presence of isophthalate groups and the coordination modes of the carboxylate functions. The strong absorption at 1714 cm^{-1} can be assigned to the stretching vibration of the protonated carboxyl group (COOH). Of three strong characteristic peaks at 1572, 1441, and 1398 cm^{-1}, the one at 1572 cm^{-1} is attributed to $\nu_{as}(COO)$ of all the carboxylate groups, while the peaks at 1441 cm^{-1} and 1398 cm^{-1} may be assigned to $\nu_s(COO)$ of the bidentate carboxylate groups and the unidentate carboxylate group, respectively, since it is known that the separation Δ ($\Delta = \nu_{as} - \nu_s$) is smaller in the former (131 cm^{-1}) than in the latter (174 cm^{-1}).[8]

Thermogravimetric analysis (TGA) under ambient conditions (Figure S1) shows an initial weight loss of 3.31% from 114 to 155 °C corresponding to the removal of all lattice water molecules per formula unit (calcd. 3.82%). The framework starts to decompose over 343 °C, with a total weight loss of 78.92% (calcd. 78.14%) for the successive elimination of all the organic components to yield MnO (calcd. 18.04%) at about 699 °C. A weight gain occurs at higher temperature, which may be due to a partial oxidation of MnO by air, in agreement with a previous observation.[9]

Heating–cooling and dehydration–hydration experiments have been carried out according to the TGA results and monitored by X-ray powder diffraction techniques. As shown in Figure 1, after the complex is dehydrated at 160 °C for 3 h, some characteristic peaks disappear, but the anhydrous compound still retains crystallinity as hinted by the existence of some weakened characteristic X-ray powder diffraction peaks. However, after the anhydrous sample is rehydrated, the diffractogram displays almost the same diffraction pattern as the original, thus indicating that the process is reversible. On the other hand, if the dehydrated sample is soaked in methanol, acetonitrile, or ethanol, solvent resorption and recovery of the original peaks do not occur perceptibly, in contrast to the behavior demonstrated in Figure 1e–g. This indicates that the exchange of water molecules with some other solvents can not be demonstrated.

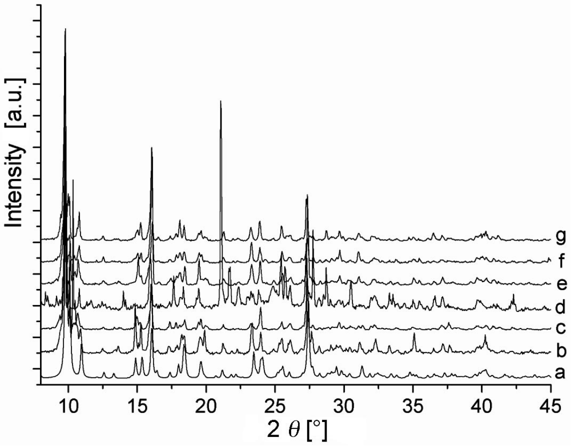

Figure 1. X-ray powder diffraction patterns for the complex: (a) calculated from single-crystal data, (b) taken from the bulk material at room temperature, (c) after heating at 160 °C for 3 h, (d) after rehydration of sample c for 36 h, (e) after soaking sample c in MeOH for 36 h, (f) after soaking sample c in MeCN for 36 h, (g) after soaking sample c in EtOH for 36 h.

Description of the Structure

Single-crystal X-ray diffraction analysis reveals that the structure of this polymer possesses a one-dimensional, ladder-like framework composed of the linear trimetallic cluster containing two five-coordinate and one six-coordinate manganese centers. As shown in Figure 2, the three Mn^{II} atoms, with an inversion on Mn2 (Mn1···Mn2 3.460(2) Å], are triply bridged by three carboxylate groups (two in $\mu_{1,3}$-bidentate modes and the third through just one oxygen atom) from two symmetry-related ip dianion ligands and one Hip monoanion ligand. The Hip monoanion functions as a simple monocarboxylato ligand bridging through its

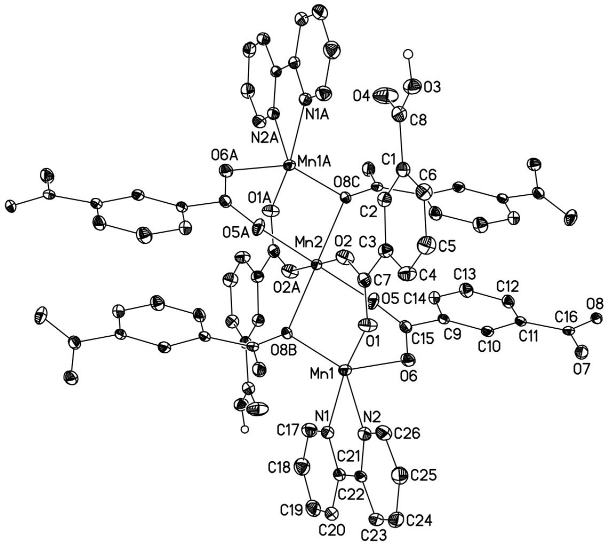

Figure 2. Local coordination environments of the Mn^{2+} centers in the complex (ellipsoids at 30% probability; symmetry codes: A: $-x + 1, -y + 1, -z + 1$; B: $x + 1, y, z$; C: $-x, -y + 1, -z + 1$); hydrogen atoms, except for that of the protonated carboxylate group, are excluded for clarity.

Table 1. Selected bond lengths [Å] and angles [°] for the complex.

Bond lengths			
Mn1–O1	2.090(3)	Mn2–O2	2.122(3)
Mn1–O8B[a]	2.183(2)	Mn2–O5	2.124(2)
Mn1–O6	2.205(2)	Mn2–O8B	2.238(2)
Mn1–N2	2.230(3)	O3–C8	1.326(5)
Mn1–N1	2.250(3)	O4–C8	1.196(5)
Bond angles			
O1–Mn1–O8B	103.50(10)	N2–Mn1–N1	73.50(11)
O1–Mn1–O6	94.05(11)	O2A–Mn2–O2	180.0
O8B–Mn1–O6	111.20(10)	O2A–Mn2–O5	86.78(11)
O1–Mn1–N2	89.10(11)	O2–Mn2–O5	93.223(11)
O8B–Mn1–N2	143.05(10)	O2–Mn2–O8B	90.94(10)
O6–Mn1–N2	102.19(10)	O5–Mn2–O8B	85.58(10)
O1–Mn1–N1	162.58(11)	O2–Mn2–O8C	89.06(10)
O8B–Mn1–N1	90.46(10)	O5–Mn2–O8C	94.42(10)
O6–Mn1–N1	90.45(10)	O8B–Mn2–O8C	180.0

[a] Symmetry codes: A: –*x* + 1, –*y* + 1; –*z* + 1; B: *x* + 1, *y*, *z*. C: –*x*, –*y* + 1, –*z* + 1.

deprotonated $\mu_{1,3}$-carboxylate group (Mn1–O1 2.090(3) Å and Mn2–O2 2.122(3) Å], and the protonated carboxyl group is freely appended. The central Mn atom is octahedrally coordinated by six carboxylate oxygen atoms, while two bidentate bipy ligands each cap the terminal Mn atoms (Mn–N 2.250(3) and 2.230(3) Å], completing the less common trigonal bipyramidal coordination on the high spin d^5 Mn^{2+} ions (Table 1).

The most remarkable structural feature of the complex is that the trimetallic cluster is further polymerized through the doubly deprotonated ip ligands in a head-to-tail fashion to yield a regular molecular ladder: the linear trimanganese units are the parallel rungs, and the ip ligands are the upright parts on both sides (Figure 3). To the best of our knowledge, this polymer represents the first example of a one-dimensional, ladder-like framework constructed from linear trimetallic clusters formed and further linked together by isophthalato ligands, though several structures of two-dimensional polymers based on linear tricopper or trinickel units have recently been described.[10] It is also worth noting that the ip dianion displays a newly observed binding mode as a terdentate μ_4-ligand to bind four Mn^{II} atoms, employing both carboxylate groups, one of which bridges through one $\mu_{1,3}$-carboxylate group (Mn1–O6 2.205(2) Å and Mn2–O5 2.124(2) Å], and the other bridges through one $\mu_{1,1}$-carboxylate group (Mn1–O8B 2.183(2) Å and Mn2–O8B 2.238(2) Å], though various other more complicated binding modes have been outlined before.[7a]

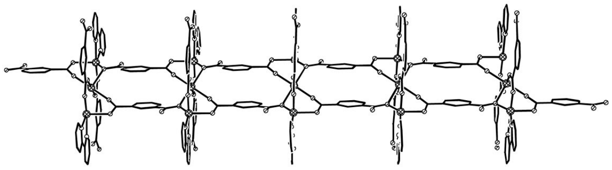

Figure 3. A view of the ladder-like double-chain structure extended along the *a* axis.

The interesting supramolecular network topology and crystal packing motif are also observed in the crystal structure. One strong hydrogen bond (O3–H3A···O6# 2.658 Å, #: *x*, *y* – 1, *z*) links the protonated carboxylate oxygen (O3) and the carboxylate oxygen (O6) of symmetry-related polymer chain to afford a beautiful stepped, two-dimensional, hydrogen-bonded network sheet with two kinds of nearly rectangular grids A and B (Figure 4). These hydrogen-bonded sheets are stacked in a parallel fashion, without interpenetration and displacement, to afford two kinds of open, nearly rectangular channels running along the *c* axis, which selectively accommodate water (O10) molecules and water (O9) dimers (O9–H9B···O9# 2.816 Å, #: –*x*, –*y* + 1, –*z* + 2), respectively (Figure 5 and S2). Interestingly, each one of the two lattice water molecules forms straight-chain water arrays within the respective host channels (Figure S3), and the water (O9) dimers also contact the host chain framework through weak O9–H9A···O7 hydrogen bonds (3.068 Å).

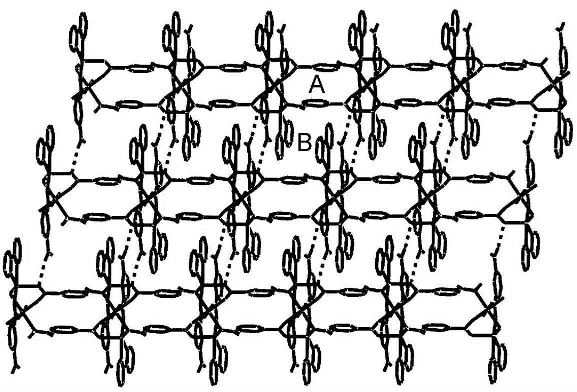

Figure 4. A view of stepped, hydrogen-bonded, 2D sheet (the hydrogen bonds, O3–H3A···O6# 2.658 Å, #: *x*, *y* – 1, *z*, are shown as dotted black lines); A and B denote two different kinds of grid regions.

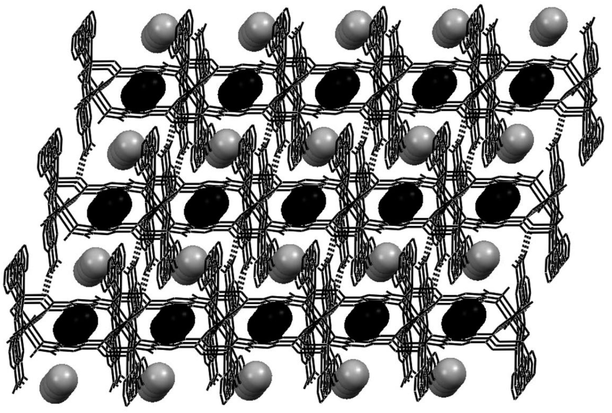

Figure 5. The packing of the H-bonded grid sheets viewed along the *c* axis, showing the formation of two kinds of open channels selectively encapsulating water (O10) molecules and water (O9) dimers; O9 and O10 are shown as space-filling objects and are colored in black and grey, respectively.

Magnetic Properties

As shown in Figure 6, the room-temperature μ_{eff} value (10.09 μ_B) is close to the expected value (10.25 μ_B) for three Mn^{II} ions uncoupled with $S_i = 5/2$ and $g_i = 2$ each. As temperature is lowered, the value of μ_{eff} decreases continuously down to 5.92 μ_B at 5 K, the low-temperature μ_{eff} being equivalent to one uncoupled Mn^{II} ion. This behavior is characteristic of significant antiferromagnetic interaction within the complex with a ground state of $S = 5/2$.[11]

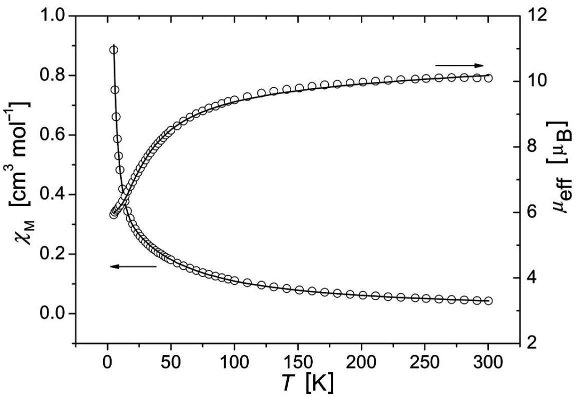

Figure 6. Plots of observed magnetic susceptibilities (χ_M) and effective magnetic moments (μ_{eff}) vs. T for the complex; the solid lines represent the calculated values.

According to the structural description, two types of magnetic exchange interactions may occur within the polymer: the intracluster interaction through the short carboxylato bridges and the intercluster interaction through the long ip ligand. Thus, it is possible to interpret the observed magnetic behavior by using the modified analytical expression in Equation (1). The expression is derived by combining the linear trimanganese(II) model [$\hat{H} = -J(\hat{S}_1 \cdot \hat{S}_2 + \hat{S}_2 \cdot \hat{S}_3)$, the interaction between two terminal Mn ions separated by above 6.9 Å is ignored for simplicity in computing] and the molecular field approximation for estimating intercluster interactions.

$$\chi_M = \chi_{\mathrm{tyi}}/(1 - zJ'\ \chi_{\mathrm{tyi}}/Ng^2\beta^2) + \mathrm{TIP} \qquad (1)$$

Taking into account the TIP term, a satisfactory fitting result with parameters $J = -4.02\ \mathrm{cm}^{-1}$, $zJ' = -3.22 \times 10^{-2}\ \mathrm{cm}^{-1}$, $g = 2.02$, $\mathrm{TIP} = 3.0 \times 10^{-3}$, and the agreement factor $R = 1.49 \times 10^{-4}$ is obtained in the full temperature range. The relatively large main J value falls in the normal range (–3.40 to –5.6 cm^{-1}) for triply carboxylato-bridged Mn^{II} compounds,[6,12] implying the perceptible existence of antiferromagnetic coupling between the Mn^{II} ions within the trimetallic cluster. The small zJ'/J ratio indicates that it is appropriate to use the mean molecular field approximation here.[13]

Conclusions

In summary, we have demonstrated a new metal–organic coordination polymer that possesses a one-dimensional, ladder-like chain structure consisting of trimanganese cluster building units formed and further linked together by isophthalato ligands, in which a terdentate μ_4-binding mode for the isophthalato ligand bridging between the trimanganese clusters is newly observed. Furthermore, the analysis of magnetic properties reveals that the intra-trimanganese-cluster coupling interactions between the Mn^{II} centers are perceptibly antiferromagnetic, like those in structurally similar discrete clusters. Thus, this study represents a successful preliminary attempt with respect to the initially intended introduction of the cluster properties to the polymeric framework. In order to advance toward our goal of developing new cluster-based extended systems with intriguing physical properties, it may be necessary to tune the cluster moiety as the building unit.

Experimental Section

General Remarks: All chemicals were of reagent grade and used as received. Elemental analyses were performed with a Vario EL III CHNOS element analyzer. Infrared spectra were recorded with a FTS-40 spectrophotometer by using pressed KBr pellets. Thermogravimetric analysis (TGA) was carried out with a NETZSCH STA449C thermal analyzer at a heating rate of 10 °C min^{-1} under ambient conditions. X-ray powder diffraction analyses were performed by using a RIGAKU DMAX2500PC X-ray diffractometer with Cu-K_α radiation (λ = 1.5418 Å) over the range 2θ from 5° to 60°, at steps of 0.05° at room temperature. Variable-temperature magnetic susceptibility (5–300 K) was measured with a model CF-1 superconducting magnetometer in a 10-kG applied field while the crystalline sample was kept in the capsule for weighing. Diamagnetic corrections were estimated by using Pascal's Table.

$[Mn_3(ip)_2(Hip)_2(bipy)_2]_n \cdot 2.5nH_2O$: 2,2′-bipyridine (2 mmol, 0.31 g) in ethanol (10 mL) was added to an aqueous solution (15 mL) comprising $Mn(OAc)_2 \cdot 4H_2O$ (2 mmol, 0.50 g) and isophthalic acid (2 mmol, 0.34 g), with continuous stirring. Acetate buffer (20 mL, 1 M) was then added to the above-mentioned yellow suspension, and the pH value was adjusted to 4 with glacial acetic acid. The resulting mixture was transferred into a 100-mL round-bottomed flask and heated to reflux for one week or so, during which time yellow crystals deposited in 0.32 g yield (41% based on Mn). The pH value of the mother liquor remained essentially unchanged. $C_{52}H_{39}Mn_3N_4O_{18.50}$ (1180.69): calcd. C 52.90, H 3.33, N 4.74; found C 53.02, H 3.20, N 4.69. IR: $\tilde{\nu}$ = 3500 (br. s), 3024 (m), 1714 (s), 1614 (s), 1603 (s), 1572 (s), 1473 (m), 1441 (s), 1398 (s), 1352 (s), 1309 (w), 1242 (s), 1161 (m), 1080 (w), 1041 (w), 1018 (m), 827 (w), 768 (m), 748 (s), 737 (s), 714 (m), 687 (m), 650 (w), 629 (w), 523 (m), 444 (w), 426 (w), 413 (m) cm^{-1}.

X-ray Crystallography: Diffraction data for the complex were collected at 295(2) K by using a Siemens Smart CCD area-detector diffractometer with graphite monochromated Mo-K_α radiation (λ = 0.71073 Å) in the ω-scan mode. Data reduction and cell refinement were performed with the SAINT program,[14] and the absorption correction was carried out by using the SADABS program.[15] The structure was solved by direct methods and subsequent difference Fourier syntheses, and refined on F^2 by the full-matrix least-squares methods with the SHELXTL-97 program package.[16] All non-hydrogen atoms were refined anisotropically. Aromatic H atoms were placed in calculated positions and treated as riding atoms, while the H atoms on both the water O9 and the carboxyl O3 were located from the different Fourier maps. Considering that the water O10 resides on a crystallographic special site and displays some disorder, no effort was made to add H atoms to it, and a site occupancy of 0.25 was estimated for it.

Crystal Data for the Complex: $C_{52}H_{39}Mn_3N_4O_{18.5}$, M_r = 1180.69, triclinic, space group $P\bar{1}$, a = 9.8351(1) Å, b = 11.6698(3) Å, c = 12.3197(2) Å, α = 98.058(1)°, β = 112.390(1)°, γ = 102.002(1)°, V = 1240.61(4) Å^3, Z = 1, $D_{calcd.}$ = 1.580 $g\,cm^{-3}$, $F(000)$ = 602, μ = 0.835 mm^{-3}, R = 0.0481 and Rw = 0.1103 for 3076 observed reflections with $I > 2\sigma(I)$.

CCDC-220084 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): TGA and DSC curves for the complex and two additional structure plots.

Acknowledgments

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