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Synthesis and structural studies on new $M^{II}X_2L_2$ dihalocomplexes of 1-methyllumazine and 1,6,7-trimethyllumazine. Crystal structure of copper(II) and palladium(II) complexes

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Abstract

In order to continue our studies in coordination chemistry with pteridine derivatives, four new complexes with general formula $M^{II}X_2(\text{pteridine})_2 \cdot nH_2O \cdot mCH_3CN$ (M = Cu, Pd, Pt) have been synthesized by reaction of 1-methyllumazine (MLM) and 1,6,7-trimethyllumazine (MLMD) and different halide salts in acetonitrile solutions. These compounds have been characterized by means of analytical techniques (elemental analysis and TG), spectral methods (IR, ^{13}C and ^{1}H NMR, UV–Vis–NIR, EPR) and magnetics measurements. Single-crystal X-ray diffraction studies have been developed on the $[CuCl_2(MLM)_2]$ and $[PdBr_2(MLM)_2]$ complexes. In the complex Cu/MLM, a six-coordinated environment around metal ion is shown, with two pteridine ligands behaving in a bidentante manner through N5/O4 atoms being the other positions occupied by two chlorine atoms. The molecular unit of the compound Pd/MLM shows an ion Pd(II) linking to two bromide ions placed in a *trans* position, and two N5 atoms of two organic ligands, exhibiting a square-planar geometry as it is usual in complexes with d^8-configuration ions.

Keywords: Crystal structures; Complexes; Pteridine; Lumazine

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1. Introduction

Pteridines are a widely distributed class of compounds that have been isolated from many living systems, including amphibia, fish, microorganisms, insects and mammals [1,2]. However, despite the ubiquitous occurrence of pteridine derivatives in all living cells, their biological functions are not yet fully understood. It is known that several unconjugated pteridines function as pigments as well as biochemically important cofactors involving oxidative hydroxylation reactions [3]. In this way, some pteridines, such as biopterin, tetrahydrofolic acid, riboflavin and molibdopterin are relevant because they are known to function as cofactors in key steps of enzymatic redox and C1 transfer processes in all kind of living organisms [4]. Besides, recent investigations have pointed out that according to their chemical structures, pteridine derivatives may act as scavengers and enhancers of several radical-mediated phenomena [5–7].

On the other hand, since several pterins as cofactors in biological redox reactions are associated with metal ions and contribute to electron transfer, information on pterin–metal interactions may give some clues about the roles of metal ions in utilization of dioxygen and concomitant electron transfer in relevant enzymatic reactions [8].

In this way, many metal–pteridine complexes have been investigated to mimic both the metal environment and reactivity of the metal role of enzymes, and some of them have been characterized by X-ray diffraction method. In most cases, data from NMR and IR spectroscopy and from the available structural analyses

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of this kind of compounds show the quelation mode of the pteridine unit through the exocyclic oxygen atom and a pyrazine ring nitrogen atom. This O,N-chelation mode of the pteridine unit is also the same coordination mode observed in metal complexes of flavins and isoalloxazines [9].

In connection to this, our research program is focused to the structural characterization of metal complexes with lumazine methylated derivatives. We have already published the molecular and crystal structure of several complexes $[ML_2(H_2O)_2]X_2$ and $[MLX_2]$ (where X = nitrate [10–12], perchlorate [13–15], halide [16,17]) containing 1-methyllumazine (MLM), 1,6,7-trimethyllumazine (MLMD), 1,3-dimethyllumazine (DLM) or 1,3,6,7-tetramethyllumazine (DLMD) as ligands. In this paper, we now report the study of four new $M^{II}X_2L_2$ complexes where M = Cu, Pd and Pt, L = 1-methyllumazine (MLM) or 1,6,7-trimethyllumazine (MLMD) and X = Cl^- or Br^-.

2. Experimental

2.1. Synthesis of the complexes

The ligands MLM and MLMD were obtained according to literature procedures [18] and characterized through analysis, ^{1}H NMR and IR spectroscopy [19].

Both MLM and MLMD ligands were able to form coordination compounds with formula $M^{II}X_2L_2 \cdot nH_2O \cdot mC_2H_3N$ (M = Cu, Pd and Pt; X = Cl^- or Br^-).

The formation of the $[CuCl_2(MLM)_2]$ complex was achieved at 40 °C in a copper(II) chloride/ligand molar ratio 2/1 (0.2 mmol copper), after several hours of reaction in MeCN (40 ml). Some days later, crystals suitable for XRD analysis were isolated.

The new Pd and Pt complexes described in this study were obtained by reaction of K_2MCl_4 (0.1 mmol) and pteridine ligand (M/L = 1:1) heating at 40–50 °C in MeCN (Pd/MLMD) or water–MeCN (Pd/MLM and Pt/MLMD) solutions (40 ml). For the Pd/MLM complex after some minutes of reaction, 1 ml of concd. aq. HBr was added and the red resultant solution was stirred during some hours. In all cases, after standing at room temperature (r.t.) for several days, the solutions gave different solids that were filtered off, washed with a small amount of ethanol and air dried. As in the copper complex, the compound $PdBr_2(MLM)_2$ was obtained as single crystals suitable for X-ray diffraction. Their molar conductance values in DMF solution indicate non-electrolytic behaviour. The analytical data are as follows (%): $CuCl_2(MLM)_2$ (green): *Anal.* Found: C, 34.01; H, 2.62; N, 22.98. Calc.: C, 34.26; H, 2.47; N, 22.84%. $PdBr_2(MLM)_2$ (red): *Anal.* Found: C, 26.42; H, 2.03; N, 17.24. Calc.: C, 27.00; H, 1.94; N, 18.00%. $PdCl_2(MLMD)_2 \cdot H_2O$ (brown): *Anal.* Found: C, 35.90; H, 3.63; N, 18.90. Calc.: C, 35.56; H, 3.65; N, 18.44%. $PtCl_2(MLMD)_2 \cdot C_2H_3N$ (yellow): *Anal.* Found: C, 32.72; H, 3.25; N, 18.10. Calc.: C, 33.38; H, 3.22; N, 17.52%.

2.2. Instrumentation

Microanalyses of C, H and N were performed in a Fisons-Instruments EA-1008 apparatus; the water content of the complexes was determined from the TG plot. TG and DSC studies were carried out under pure air on a SHIMADZU system (TGA-50 thermobalance and DSC-50 differential scanning calorimeter) using approximately 5 mg of sample and a 20 °C min^{-1} heating rate in the TG and 10 °C min^{-1} in the DSC plots. IR spectra were measured on a Perkin–Elmer FT-IR 1760-X (KBr pellets, 4000–400 cm^{-1}) and on a Bruker FT-IR VECTOR 22 spectrophotometer (polyethylene pellets, 600–180 cm^{-1}). ^{13}C and ^{1}H NMR spectra were recorded using a Bruker DPX-300 apparatus (DMSO-d_6 solutions). The EPR spectra were obtained in the X-band at r.t. on a Bruker ESP 300E apparatus, with a microwave frequency of 9.79 GHz and a modulation frecuency of 100 kHz. Magnetic measurements were carried out on a Manics DSM-8 system between 77 and 290 K. Reflectance diffuse spectra (200–1200 nm) were recorded on a Perkin–Elmer UV–Vis–NIR Lambda-19 machine using a $BaSO_4$ pellet as reference.

2.3. Crystallography

Crystal data and structure refinement details are given in Table 1. The structure was solved by direct methods using the SHELXTL program package [20]. Refinement was carried out using SHELXL-97 employing full-matrix least-squares methods on F^2. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in their ideal positions.

3. Results and discussion

3.1. X-ray structural study of the complexes

A molecular drawing representing $[CuCl_2(MLM)_2]$ molecular unit together with the atom labelling scheme is given in Fig. 1; distances and angles around the metal ion are given in the Table 2. The X-ray structure (Fig. 1) shows a six-coordinated environment around metal ion with two pteridine ligands behaving in a bidentante manner through N5/O4 atoms forming five-membered chelate rings and the other positions being occupied by two chlorine atoms.

In the *trans*-$[CuCl_2(MLM)_2]$ coordination polyhedron, the equatorial plane consists of two N5 atoms (Cu–N5, 1.997(2) Å) and two chlorine atoms (Cu–Cl,

Table 1
Crystallographic and refinement data

Compound	Cu/MLM	Pd/MLM
Empirical formula	$C_{14}H_{12}Cl_2CuN_8O_4$	$C_{14}H_{12}Br_2N_8O_4Pd$
Formula weight (g mol^{-1})	490.76	622.54
Temperature (K)	173 (2)	293(2)
Wavelength (Å)	0.71070	0.71073
Crystal system	monoclinic	triclinic
Space group	$P21/a$	$P\bar{1}$
Unit cell dimensions		
a (Å)	7.7760(5)	6.5185(9)
b (Å)	11.3030(7)	7.5120(1)
c (Å)	10.5310(7)	10.7736(9)
α (°)		94.35(1)
β (°)	106.376(3)	106.036(8)
γ (°)		109.33(1)
V (Å^3)	888.0(1)	470.2(1)
Z	2	1
D_{calc} (Mg m^{-3})	1.835	2.198
Absorption coefficient (mm^{-1})	1.575	5.278
F(000)	494	300
Crystal size (mm)	$0.25 \times 0.10 \times 0.10$	$0.5 \times 0.1 \times 0.02$
Diffractometer	Kappa CCD	Siemens P4
Radiation	Mo Kα	Mo Kα
θ Range for data collection (°)	2.02–27.16	2.00–29.99
Index ranges	$0 \le h \le 9$, $-14 \le k \le 14$, $-13 \le l \le 12$	$-1 \le h \le 9$, $-10 \le k \le 10$, $-15 \le l \le 14$
Reflections collected/independent	8467/1948	3372/2716
R_{int}	0.0646	0.0273
Weighting scheme, $w = 1/[\sigma^2(F_o^2)+(xP)^2+yP]$ [a]	$x = 0.0399/y = 0.1143$	$x = 0.15/y = 0.3$
Data/restraints/parameters	1948/0/151	2716/0/134
Final R indices $[I > 2(I)]R/wR^2$	0.0387/0.0867	0.0720/0.1998
R indices (all data) R/wR^2	0.0730/0.0966	0.0953/0.2209
Goodness-of-fit on F^2	1.054	1.074
Largest difference peak/hole (e Å^{-3})	0.408/−0.658	2.915/−2.364

[a] $P = (F_o^2 + 2F_c^2)/3$.

Table 2
Bond lengths (Å) and angles (°) around the metal ion in the crystal structures of $[CuCl_2(MLM)_2]$ and $[PdBr_2(MLM)_2]$

	Cu/MLM/Cl	Pd/MLM/Br
Bond lengths		
M–O(4)	2.380(2)	2.832(6)
M–N(5)	1.997(2)	2.011(6)
M–X	2.3159(7)	2.4432(8)
Bond angles		
N(5)–M–O(4)	77.85(8)	70.2(2)
X–M–N(5)	90.05(7)	90.4(2)
X–M–O(4)	92.47(5)	86.3(2)

2.3159(7) Å). The geometry around the Cu(II) ion exhibits Jahn–Teller effect, in which the polyhedron is elongated through O4–Cu–O4′ axis. This tetragonal elongation is consistent with a $d_{x^2-y^2}$ ground state of Cu(II) ion. Although the distance Cu–O4 is larger than in similar complexes [21], it is shorter than that needed to force a square-planar complex ($R = 1.19$).

The lumazine ligands are virtually planar and roughly coplanar with the five-membered chelate ring (1.76°); the distance between the ion Cu(II) and the pteridine plane is only 0.093 Å. The greatest deviations from the mean plane in the lumazine derivative occur in the N3 for the endocyclic atom (0.033 Å) and the C1 for the exocyclic one (0.078 Å).

The bonding parameters for the organic ligands are very close to those found for previously reported bidentate lumazine derivatives [10–17], indicating a high electronic delocalization, being the C2–O2 distances a little shorter than that of C4–O4 because of the involvement of the O4 atom in the coordination.

Despite this complex shows a very similar molecular structure to the $[CuCl_2(DLM)_2]\cdot 2H_2O$ one [17], the presence of a hydrogen atom attached to the N3 position causes fundamental differences in the hydrogen-bonding scheme. Thus, in the H-bonded chain-like structure of $[CuCl_2(DLM)_2]\cdot 2H_2O$ [17], the H-bonds are established only between the water molecules and the coordinated chlorine atoms, whereas in the $[CuCl_2(MLM)_2]$ structure the existence of the N3–H available for H-bonding designs a bidimensional H-bond network parallel to *ab* plane. Both organic ligands and M–Cl bonds are angled with this plane by 48 and 39°, respectively (Fig. 2).

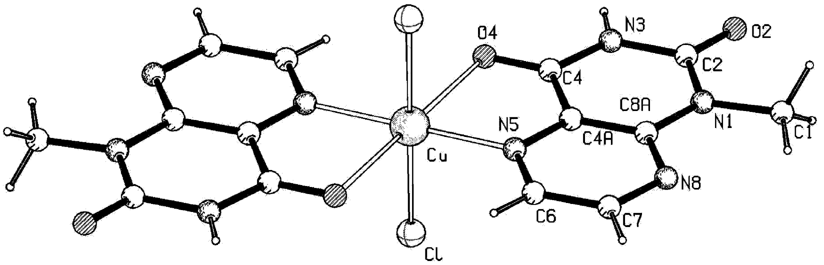

Fig. 1. Molecular drawing and numbering scheme for the monomeric unit of *trans*-$[CuCl_2(MLM)_2]$.

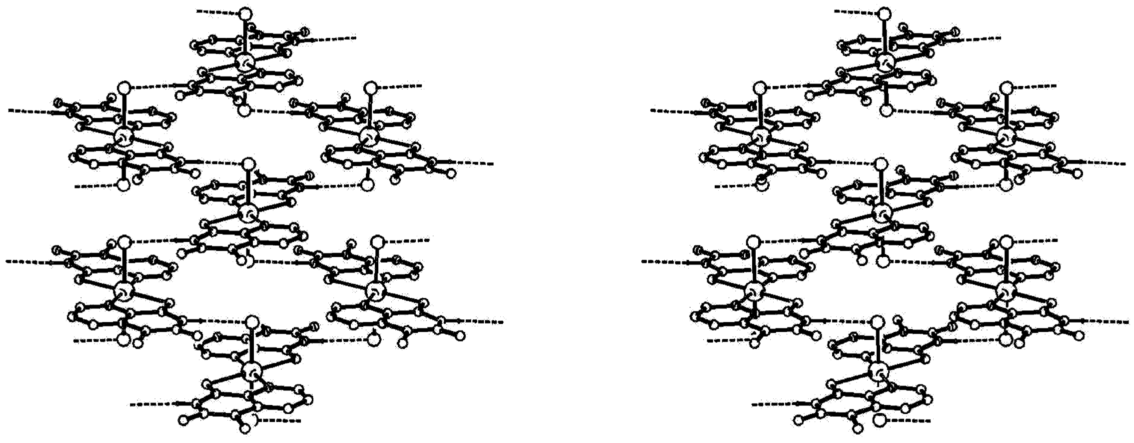

Fig. 2. Stereoview of the H-bond network of the complex [$CuCl_2(MLM)_2$]. Hydrogen bonds are as follows N3···Cl (1/2+x, 1/2−y, z), 3.212 Å and ∠ N3–H3···Cl, 174°.

The molecular unit of the [$PdBr_2(MLM)_2$] complex with the numbering scheme is shown in Fig. 3. Selected bond distances and angles are listed in Table 2. The structure shows a Pd(II) ion linking to two bromide ions placed in a *trans* position [d(Pd–Br); 2.4432(8) Å] and two N5 atoms [d(Pd–N5); 2.011(6) Å] of two organic ligands. As it is found in similar complexes, the pteridine ligands should behave in a bidentante manner through N5/O4 atoms; but in this palladium complex, the location of O4 atom at 2.832(6) Å and its related angles, are indicative of a very weak Pd–O interaction [22]. However, the primary coordination sphere would be of the type PdN_2Br_2 with a square-planar geometry as it is usual in complexes with d^8-configuration ions [23].

The H-bond pattern in the Pd/MLM complex is similar to those found in the free MLM; however, the presence of two pteridine group *per* molecular unit allows the establishement of linear chains. In Fig. 4, the *zig-zag* chain established by H-bonds though N3–H3···O2 atoms (1−x, −y, −z) has been displayed. The distance donor–acceptor and the corresponding angle are 2.90(1) Å and 177°, respectively. The chains generated by hydrogen bonds are packed following the [0 1 1] direction.

3.2. Thermal and spectral studies

The study of the thermal decomposition of these compounds in air has been carried out from their TG and DSC plots. In the complexes [$CuCl_2(MLM)_2$] and [$PdBr_2(MLM)_2$] the corresponding TG plots confirm their anhydrous character. In the other two complexes the water and acetonitrile molecules are lost in one step in the TG plot at temperatures down to 250 °C. However, in both cases, DSC curves show two different endothermic effects that may be due to the anhydrous complexes fussion. The pyrolysis begins after the loss of the solvent and finishes at 600 °C, leaving as final residue the palladium oxide ($PdCl_2(MLMD)_2 \cdot H_2O$) and the metallic platinum ($PtCl_2(MLMD)_2 \cdot C_2H_3N$), respectively. The pyrolysis in the complexes Cu/MLM and Pd/MLM finishes at a higher temperature (around 900 °C), being the corresponding oxides collected as final residues, as it has been corroborated from the corresponding infrared spectrum.

The most significant IR bands complexes are similar to those found in other compounds with lumazine derivatives. They were assigned by comparing them with others reported previously for several lumazine

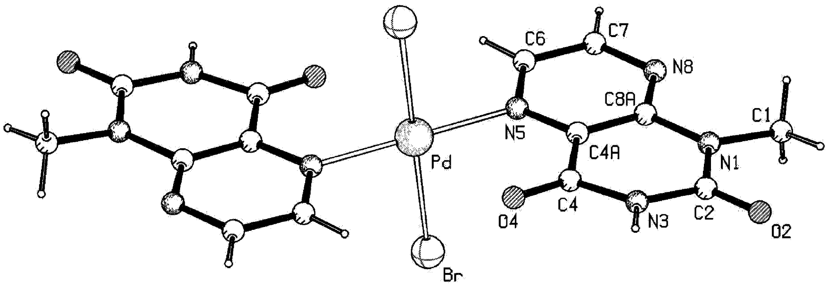

Fig. 3. Molecular drawing and numbering scheme for the monomeric unit of *trans*-[$PdBr_2(MLM)_2$].

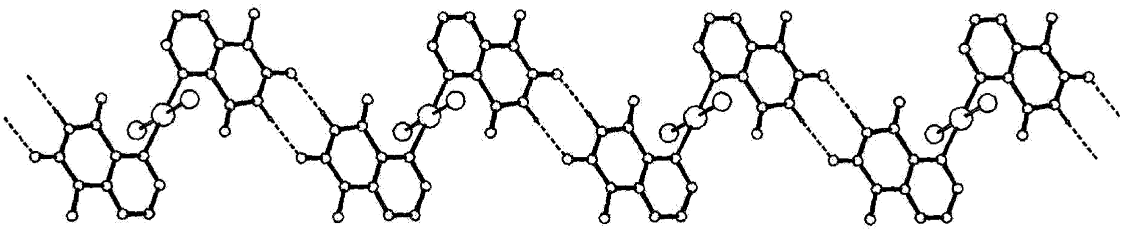

Fig. 4. View of a monodimensionally H-bonded chain of $[PdBr_2(MLM)_2]$.

derivative complexes, as well as with the IR spectra of the free ligands.

The $PdCl_2(MLMD)_2 \cdot H_2O$ complex shows a broad band at 3400 cm^{-1} attributed to the presence of lattice water. The $PtCl_2(MLMD)_2 \cdot C_2H_3N$ shows a weak $\nu(C\equiv N)$ band at 2335 cm^{-1} corresponding to the acetonitrile molecule [24].

In the four complexes studied, the infrared spectra show the ν(N–H) and ν(C–H) bands in the 3200–2800 cm^{-1} region. The bands assignable to the C=C, C=N and C=O stretching vibrations are shifted respect to their position in the spectra of uncoordinated MLM and MLMD.

The vibrational activity of carbonyl groups is coupled and appears as two bands, except in the Pd/MLM complex in which only one band can be distinguished due to the very similar distances C4=O4 (1.202(9) Å) and C2=O2 (1.20(1) Å). The higher (1700–1730 cm^{-1}) is mainly due to ν(C2=O) and the other one (1650–1680 cm^{-1}) must be assigned to ν(C4=O). In all MLM complexes, both bands are strongly shifted with respect to their position in the IR spectrum of the free ligand whereas in the MLMD complexes the shifts are significantly weaker. These displacements are due to the different H-bond scheme found in the free MLM and MLMD; thus, in the free MLM, dimeric units are produced via O2···H3–N3 hydrogen bonds, whereas in the MLMD ligand, these H-bonds are established through the O4 atom. Therefore, the involvement of the O4 atom in the coordination to the metal induces a weaker shift in the ν(C4=O) band in the MLMD complexes than in the MLM ones.

The absorption bands located at 1580 (MLM) and 1553 (MLMD) cm^{-1} in the IR spectra of the free ligands are attributed to ν(C=N) and the two bands at 1478 and 1299 cm^{-1} in the MLM and 1453 and 1285 cm^{-1} in the MLMD are assignable to $\nu(C{=}C)+\nu(C{-}N)$. These bands are shifted in the corresponding complexes, indicating the involvement of the N5 atom in coordination to the metal ion.

In the far-infrared region, one ν(M–X) ($X = Cl^-$ or Br^-) band is observed in the spectra of the Cu/MLM (256 cm^{-1}), Pd/MLM (280 cm^{-1}), Pd/MLMD (353 cm^{-1}) and Pt/MLMD (333 cm^{-1}) complexes assignable to the terminal chlorine or bromine atoms in a *trans* arrangement [25].

Within experimental error, both ^{13}C and ^{1}H NMR spectra of palladium and platinum complexes display the same signals than those of the free ligands (there are not additional signals), clearly indicating that these compounds may undergo strong solvolysis. Although, an alternative explanation based on the π-electronic density is unchanged upon coordination cannot be discarded.

The EPR spectrum of $[CuCl_2(MLM)_2]$ is of axial type where only the $g_\perp$ (2.06) value can be measured. This spectrum is consistent with a distorted tetragonal octahedral geometry around Cu(II) ion and with the single unpaired electron located in an essentially $d_{x^2-y^2}$ orbital. The electronic reflectance spectrum of this complex shows a broad and asymmetric band centred at 13 600 cm^{-1}, typical for distorted octahedral complexes [26]. This band was deconvoluted into Gaussian component bands in the visible region. Starting from a set of six peaks, computer iteration processes for experimental curves fitting were carried out to minimize the standard deviation from the calculated ones, reaching a standard deviation of approximately 0.004 absorbance units. Thus, three peaks were obtained centred at 16 400, 13 700 and 10 500 cm^{-1}; these bands are assignable to the transitions from ^2A and ^2B terms in which the fundamental ^2E term (O_h) is splitted as consequence of Jahn–Teller effect, to the ^2T term that is slightly splitted in ^2E and ^2B terms as a consequence of the distortion in the octahedra [22].

The molar susceptibility values at different temperatures have been successfully fitted to the Curie–Weiss' law ($C = 0.971$ cgsu K mol^{-1}, $r^2 = 0.9956$), where the θ value (−80.7 K) could indicate a slightly antiferromagnetic interaction. The measured μ_{eff} value (2.3 MB) differs from the spin-only moment (1.73 MB) due to the partial mixing of excited states representing orbital momentum with the ground state with no orbital contribution [27]; also, the monomeric nature found from XRD experiments is corroborated.

4. Supplementary material

Supplementary material including all atomic coordinates, anisotropic displacement parameters for non-hydrogen atoms and all interatomic distances and bond angles have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 193058 and 193059 for the compounds [$CuCl_2(MLM)_2$] and [$PdBr_2(MLM)_2$], respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1233-336033; e-mail: deposit@ ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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