

Ruthenium, osmium and rhodium complexes of polypyridyl ligands: Metal-promoted activities, stereochemical aspects and electrochemical properties

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Abstract. This article presents a brief overview of the reactions of 2,4,6-*tris*(2-pyridyl)-1,3,5-triazine (tptz) in presence of rhodium(III), ruthenium(II) and osmium(II) under various experimental conditions. Under certain experimental conditions tptz exhibits metal-assisted hydrolysis/hydroxylation at the triazine ring. However, synthetic methods have also been developed to prepare complexes with intact tptz. Molecular structures of some of the complexes, especially stereoisomers of the hydroxylated products, are established by single crystal X-ray studies. A critical analysis of all data suggests that the electron-withdrawing effect of the metal ion (L→M σ donation) is the predominant factor, rather than angular strain, that is responsible for metal-promoted reactivities. Electrochemical properties of all of these complexes have been investigated, Rh(III) complexes are excellent catalysts for electrocatalytic reduction of CO₂, and dinuclear Ru(II) and Os(II) complexes exhibit strong electronic communication between the metal centres.

Keywords. 2,4,6-*Tris*(2-pyridyl)-1,3,5-triazine; metal-assisted reactions; ruthenium(II), osmium(II) and rhodium(III)/(II) complexes; crystal structure; electrochemistry.

1. Introduction

In recent years, ruthenium(II), osmium(II) and Rh(III) complexes of polypyridyl ligands have received much attention because of their rich electrochemical and photophysical properties, and their potential applications in various supramolecular structures as electronic and photomolecular devices^{1–7}. Multinuclear systems of this kind can be developed by covalent linking of building blocks with spacers which, therefore, is the key component because the size, shape and electronic nature of the bridge controls the electronic communication between the chromophores and thereby the molecule as a whole. The ligand 2,4,6-*tris*(2-pyridyl)-1,3,5-triazine (tptz) is a potential spacer, which functions as a *bis*-bidentate or simultaneously as a tridentate and a bidentate bridging unit. The ligand tptz is believed to be stable towards nucleophilic attack and has been used as an analytical reagent for various metal ions^{8–11}. A few mono and dinuclear complexes of ruthenium(II) of tptz has also been reported^{12–14}. However, our studies reveal that under certain experimental conditions tptz undergoes various metal-assisted reactions^{15–19}. Here, we briefly account the reactivities of tptz in presence of rhodium(III), ruthenium(II) and osmium(II), stereochemistry of the products, mechanistic aspects of hydrolysis/hydroxylation and electrochemical properties.

2. Experimental

Materials, physical measurements and methods of preparation of all complexes (**1–18**) are described elsewhere^{15–18}.

3. Results and discussion

3.1 Synthesis and characterisation of rhodium(III) complexes^{15,16}

The mononuclear complexes of compositions $[\text{Rh}(\text{tptz})\text{Cl}_3]$ (**1**) and $[\text{Rh}(\text{tptz})_2](\text{ClO}_4)_3$ (**2**) were synthesised by the reaction of tptz (figure 1a) and RhCl_3 in ethanol and acetone respectively. During the synthesis of these complexes no nucleophilic attack at the triazine ring of tptz was observed. However, the reaction of the tptz and RhCl_3 in refluxing ethanol–water resulted in the hydrolysis of tptz to [bis(2-pyridyl-carbonyl)amide] anion (bpca) yielding Rh(III) as well as Rh(II) complexes, $[\text{Rh}(\text{bpca})_2][\text{PF}_6]$ (**3**) and $\text{Rh}(\text{bpca})_2$ (**4**) respectively. The tptz of complex **1** was also hydrolysed when it was treated with $[\text{Rh}(\text{tpy})\text{Cl}_3]$ in ethanol–water and resulted in the formation of Rh(III) and Rh(II) complexes, $[\text{Rh}(\text{bpca})(\text{tpy})][\text{PF}_6]_2$ (**5**) and $[\text{Rh}(\text{bpca})(\text{tpy})][\text{PF}_6]$ (**6**), respectively. Hydrolysis of the tptz of complex **2** also occurred under similar experimental conditions yielding $[\text{Rh}(\text{bpca})_2](\text{ClO}_4)$. Molecular structures of complexes **1** (figure 1b), **3** (figure 1c), **4**, **5**, and **6** (figure 1d) were established by single crystal X-ray studies. Metal ions in these complexes show octahedral geometry in which tptz/bpca function as a tridentate ligand. Rhodium(II) complexes are interesting, the bpca moiety provides the necessary structural and electronic requirement to stabilise mononuclear paramagnetic Rh(II) complexes, otherwise it is extremely difficult to prepare using polypyridyl ligands. Complexes **4** and **6** are the first examples of structurally characterised mononuclear Rh(II) complexes with polypyridyl ligands.

3.2 Synthesis and characterisation of ruthenium(II) and osmium(II) complexes^{18,19}

The reaction of $\text{Ru}(\text{bpy})_2\text{Cl}_2$ and $\text{Os}(\text{bpy})_2\text{Cl}_2$ with tptz (1:1 molar ratio) resulted in the formation of $[(\text{bpy})_2\text{Ru}(\text{tptz})](\text{PF}_6)_2$ (**7**) and $[(\text{bpy})_2\text{Os}(\text{tptz})](\text{PF}_6)_2$ (**8**), respectively. Interestingly, when similar experimental conditions were used to prepare binuclear complexes then an unexpected hydroxylation occurred at the carbon atom of the triazine ring, which resulted in the formation of $[\{\text{Ru}(\text{bpy})_2\}_2(\text{tptz-OH})](\text{PF}_6)_3$ (**9**), $[\{\text{Os}(\text{bpy})_2\}_2(\text{tptz-OH})](\text{PF}_6)_3$ (**10**) and the heterodinuclear complex $[(\text{bpy})_2\text{Ru}(\text{tptz-OH})\text{Os}(\text{bpy})_2](\text{PF}_6)_3$ (**11**). Again, hydroxylation of tptz did not occur in the dinuclear complexes $[(\text{bpy})_2\text{Ru}(\text{tptz})\text{Ru}(\text{tpy})](\text{PF}_6)_4$ (**12**) and $[(\text{bpy})_2\text{Os}(\text{tptz})\text{Ru}(\text{bpy})_2](\text{PF}_6)_4$ (**13**) when they were synthesised by the reaction of $[(\text{tpy})\text{Ru}(\text{tptz})]^{2+}$ and $\text{Ru}(\text{bpy})_2\text{Cl}_2/\text{Os}(\text{bpy})_2\text{Cl}_2$ under the above reaction conditions. However, hydroxylation of tptz occurred when an attempt was made to prepare the same compound following a different route, as the reaction of $[(\text{tpy})\text{RuCl}_3]$ and $[(\text{bpy})_2\text{Ru}(\text{tptz})]^{2+}$ under similar experimental conditions yielded $[(\text{bpy})_2\text{Ru}(\text{tptz-OH})\text{Ru}(\text{tpy})\text{Cl}](\text{PF}_6)_2$ (**14**). The trinuclear complexes without hydroxylation of tptz, $[(\text{bpy})_2\text{M}(\text{tptz})_2\text{Ru}](\text{PF}_6)_6$ ($\text{M} = \text{Ru}$ (**15**), Os (**16**)), were obtained by the reaction of $[(\text{bpy})_2\text{M}(\text{tptz})]^{2+}$ with $[\text{RuCl}_2(\text{DMSO})_4]$ (2:1 ratio) in 2-methoxyethanol. However, attempt to obtain the same compound using RuCl_3 instead of $[\text{RuCl}_2(\text{DMSO})_4]$ in ethanol–water resulted in hydroxylation of tptz. All of these complexes were characterized by analytical and spectroscopic methods^{18,19}. Molecular

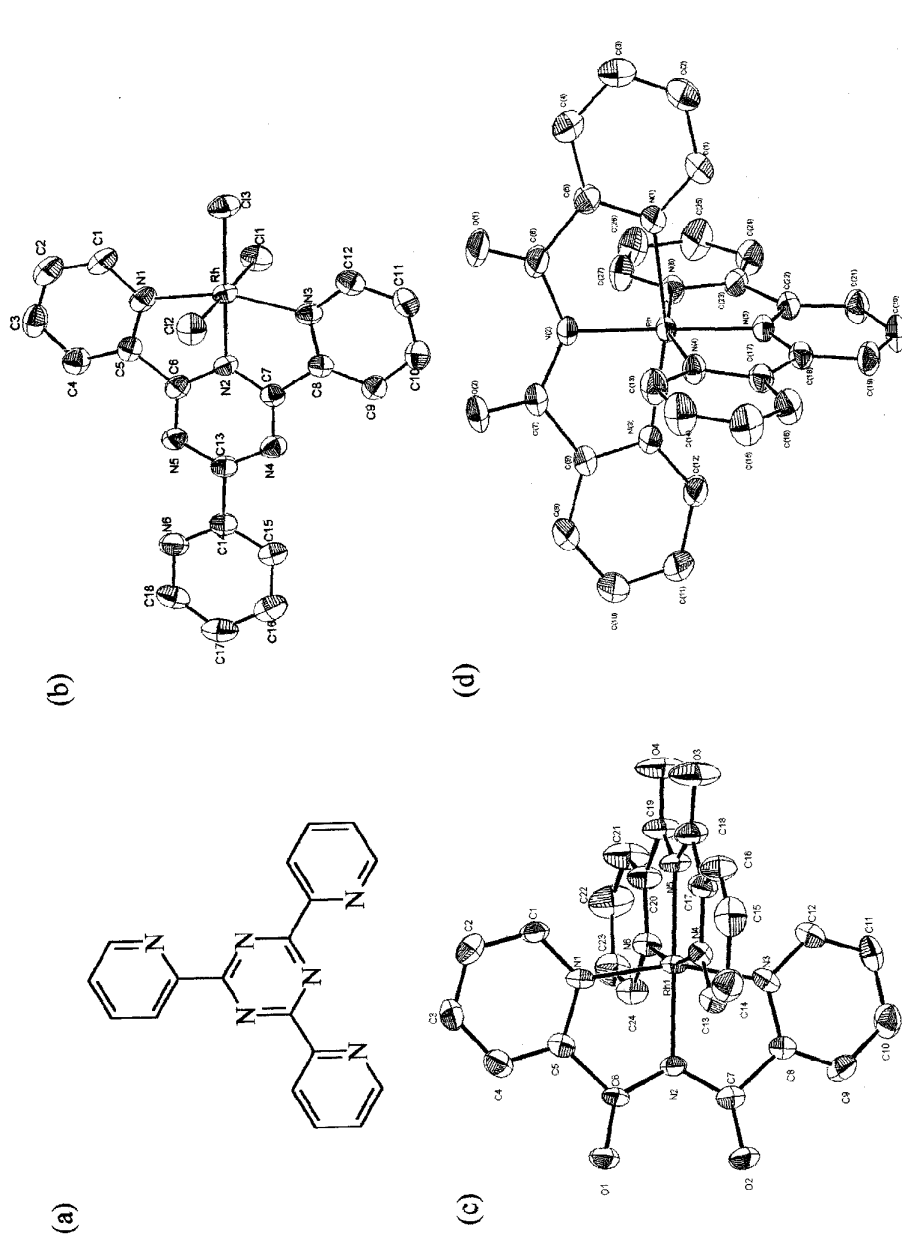


Figure 1. (a) Structure of the ligand tptz; ORTEP views of (b) $[\text{Rh}(\text{tptz})\text{Cl}]_3^+$, (c) $[\text{Rh}(\text{tpca})_2]^+$ and (d) $[\text{Rh}(\text{tpca})_2(\text{tpy})]^+$.

structures of many of these complexes were determined crystallographically and some of the structures are shown in the following section.

4. Stereochemistry of the dinuclear complexes¹⁸

Octahedral metal centres with bidentate ligands generally show stereoisomerism²⁰. The homodinuclear complexes **9** and **10**, where the coordination environments of the metal centres is equivalent, exist in two diastereoisomeric forms $\Delta\Delta$ (*meso*) and $\Delta\Delta/\Lambda\Lambda$ (*rac*), which arise due to the different orientation of the pyridyl rings with respect to the plane of the bridging ligand. Both the *meso* and *rac* isomers were isolated in pure form by repeated partial crystallisation and were characterised by ¹H NMR and crystallographic studies. The PLUTO views of the *meso* and *rac* isomers of **10** are shown in figures 2a and 2b. The optical isomers (*d* and *l*) of complex **9** are shown in figures 2c and 2d.

The NMR spectroscopy was found to be a useful technique to differentiate stereoisomers. The ¹H NMR spectra of *meso* and *rac* forms show significant difference, specially OH and some H₃ and H₆ protons (usual numbering of bipyridyl is used), due to different orientation of the pyridyl rings. The electronic spectra of *meso* and *rac* forms are similar but not the same. A slight difference in I_{\max} and molar absorption (ϵ) is observed, similar observation was also noted by Keene *et al*²¹. However, no observable difference in the electrochemistry of *meso* and *rac* isomers is noted.

5. Mechanistic aspects of the hydrolysis/hydroxylation

Triaryltriazenes are usually stable towards hydrolysis²², however, it does occur under certain experimental conditions in the presence of some metal ions. It was first observed by Lerner and Lippard in aqueous media in the presence of Cu(II)²³ and the structure of this complex with one hydrolysed tptz (bpca) was established crystallographically²⁴. On the basis of Cu–N bond distances and angles at the carbonyl carbon atoms within the chelate ring (**Aa** figure 3a) of this compound it was suggested that co-ordination of tptz induces an angular strain allowing nucleophilic attack at the carbon atoms of the triazine ring by the solvent resulting in the hydrolysis of tptz. Crystallographic data of our Ru(II) (figure 3b) and Rh(III) (figure 3c) complexes with intact tptz and also Rh(III) complexes (figure 3d) with hydrolysed tptz suggest that the angular strain experienced by Ru(II) and Rh(III) complexes are comparable and are similar to that of Cu(II) complex. Therefore, on the basis of strain factor alone one cannot explain the hydrolysis of tptz only in the Rh(III) complexes and not in the Ru(II) complex under similar experimental conditions. This suggests that the metal ion plays a major role in the hydrolysis of tptz. In the Rh(III) complexes the electron-withdrawing effect of the metal ion results in an enhanced electrophilicity on the carbon atoms (C^{d+}) adjacent to the metal-bound nitrogen atom of the triazine ring, thus making it susceptible to nucleophilic attack. In the Ru(II) complex, the metal ion has the ability to form π back-bonding with unsaturated ligands compensating partially for the σ electron-withdrawing effect. As a result, the electrophilicity on the carbon atom in question is not sufficient to make it susceptible to nucleophilic attack. The π back-bonding in the Rh(III) is apparently not effective. The crystal structures of Ru(II) and Rh(III) with intact tptz show the presence of two water molecules in the lattice at similar sites. In the Rh(III) complex, both the water molecules made short contact with the carbon atoms to be hydrolysed ($C\cdots O$; 3.026(6), 3.058(8) Å) thus making it a model close to the ‘intermediate’ of hydrolysis by nucleophilic attack.

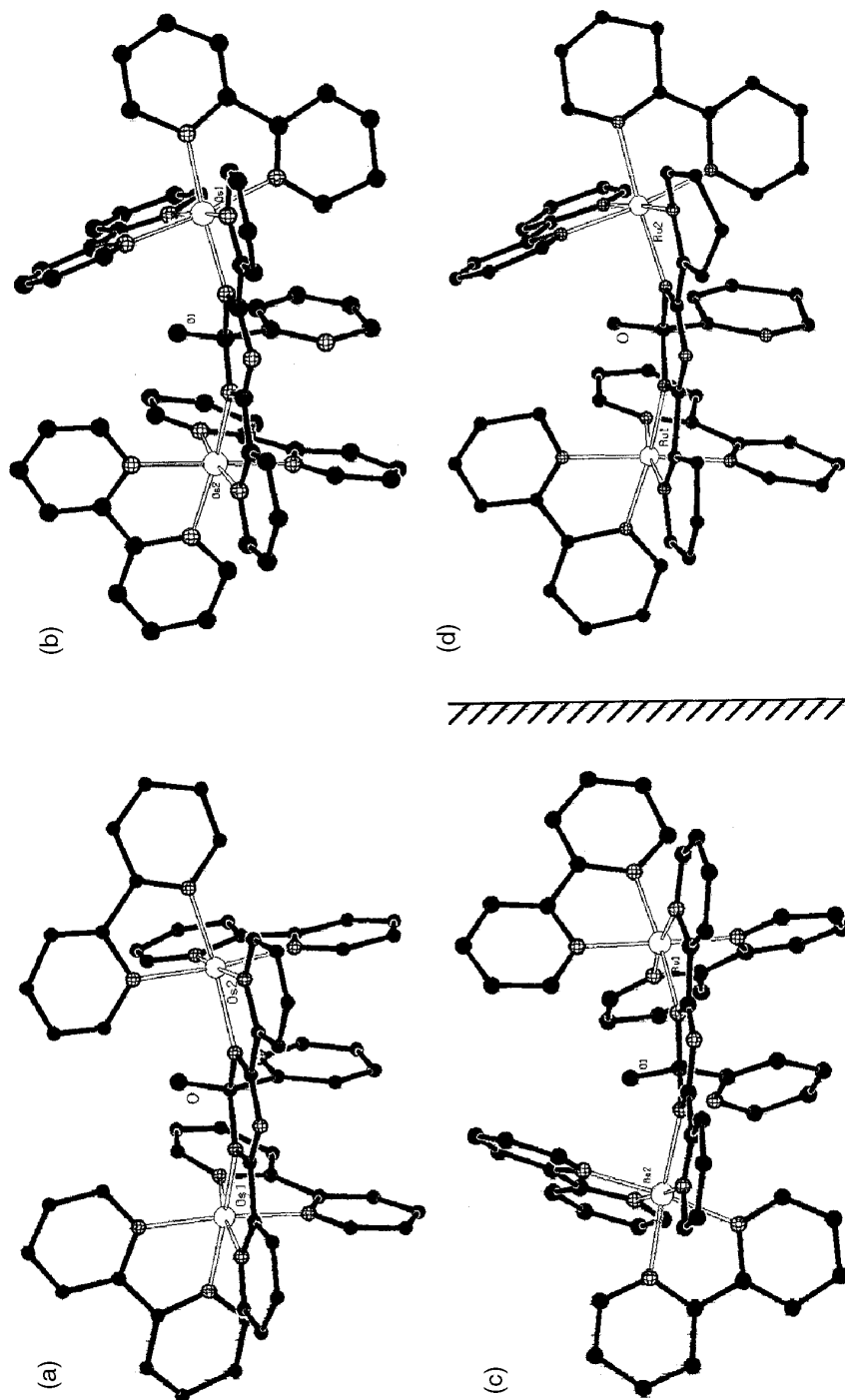


Figure 2. PLUTO views of the (a) *meso* and (b) *rac* forms of $[\text{Os}(\text{bpy})_2]_2(\text{tpiz-OH})^{3+}$; (c) and (d) are the optical isomers (d and l) of $[\text{Ru}(\text{bpy})_2]_2(\text{tpiz-OH})^{3+}$.

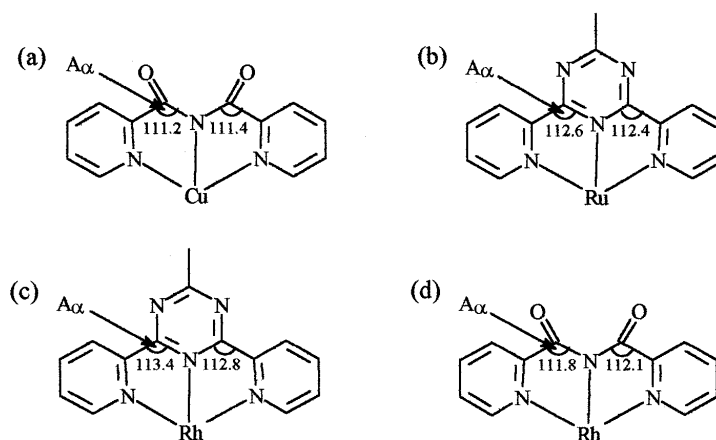


Figure 3. Drawings showing the relevant structural portions of complexes (a) $[\text{Cu}(\text{bpca})(2\text{-picolinamide})]^+$ (from ref. 24), (b) $[\text{Ru}(\text{tptz})_2]^{2+}$ (from ref. 15), (c) $[\text{Rh}(\text{tptz})\text{Cl}_3]$ and (d) $[\text{Rh}(\text{bpca})_2]^+$.

However, in the Ru(II) complex, the water molecules do not show any significant interaction with the carbon atoms ($\text{C}\cdots\text{O}$; 3.908 Å), indicating that the carbon atoms are not sufficiently electropositive to interact with the water molecule effectively.

Hydroxylation at the carbon atom of the triazine ring of tptz occurred in the binuclear complexes of Ru(II) and Os(II), where tptz is used as a spacer between the two building blocks (figure 2). Interestingly, hydroxylation at the triazine ring did not occur in the mononuclear complexes under similar experimental conditions. This difference could be due to π -back-bonding effect of metal ion. As mentioned above, this effect reduces electrophilicity on the carbon atoms, however, at least some resultant electron deficiency makes these carbon atoms electropositive (C^{d+}) to some degree. Such an effect from one metal centre may not be sufficient to make the carbon atom susceptible to nucleophilic attack but the combined effect from both sides in the dinuclear complexes possibly makes the carbon atom an electrophilic centre. As a result, hydroxylation occurs in the dinuclear complexes but not in the corresponding mononuclear ones. The other factor is the steric hindrance due to overcrowding of a number of pyridyl rings, hydroxylation creates tetrahedral geometry around the carbon atom and provides significant relief to the overcrowding.

6. Electrochemistry

Cyclic voltammograms of all of the Rh(III) complexes were recorded in argon and carbon dioxide saturated solutions. In an argon atmosphere they show a metal-based composite wave in the range -0.42 to -0.98 V (vs SCE) corresponding to $2e$ reduction ($\text{Rh(III)} \rightarrow \text{Rh(I)}$) and a ligand-based one electron redox couple. In the CO_2 saturated solution they exhibit a new cathodic peak in the potential range -1.26 to -1.44 V with a large enhancement of current, indicating electrocatalytic reduction of CO_2 . The reduction of CO_2 in DMF in the absence of catalyst occurs at a potential more negative than -2.0 V²⁵. A significant anodic shift of the reduction potential of CO_2 in presence of metal ion indicates strong electrocatalytic effect. Controlled potential CO_2 reduction catalysis

experiments were performed, the product was identified as formate and the turnover frequencies were 6.8 to 10.8 (moles of formate produced per mole of catalyst per hour).

Mononuclear Ru(II) and Os(II) complexes exhibit a metal-based oxidation ($M(II) \rightarrow M(III)$) at +1.42 and +0.97 V for Ru(II) and Os(II) respectively, and three ligand-based redox couples in the potential range -0.73 to -1.64 V. In the dinuclear complexes two metal-based one-electron oxidations and five ligand-based reductions were observed. In symmetric homodinuclear complexes, like **9** and **10**, the splitting of the metal-based oxidation wave indicates electronic communication between the metal centres and the extent of splitting reflects the degree of metal-metal interaction. The comproportionation constant (K_{com}) of 6.03×10^4 – 4.70×10^6 of the mixed valence species suggest strong electronic coupling between the metal centres. The ligand tptz has a low-lying π^* orbital; therefore, metal-metal communication through the bridge by an electron transfer mode across the low-lying π^* orbital of the bridging ligand probably occurs.

7. Conclusions

The reactions of 2,4,6-*tris*(2-pyridyl)-1,3,5-triazine with Rh(III), Ru(II) and Os(II) under various experimental conditions revealed metal-assisted unusual reactivities of the ligand. However, methods have also been developed to prepare metal complexes with intact tptz. Formation of stable mononuclear paramagnetic Rh(II) complexes is quite interesting, otherwise it is very difficult to prepare, specially with polypyridyl ligands. Isolation of the stereoisomeric forms of the dinuclear Ru(II) and Os(II) complexes and their spectroscopic and crystallographic characterization is noteworthy. For metal-promoted activities, the electron-withdrawing effect of the metal ion seems to be the predominant factor rather than angular strain. One of the important findings is that the Rh(III) complexes exhibit effective catalytic property in the electrocatalytic reduction of carbon dioxide. The electrochemical studies of the dinuclear Ru(II) and Os(II) complexes suggest strong metal-metal electronic interaction mediated by the bridging ligand. Since this ligand (tptz) shows various metal-promoted activities, therefore, in future one should be careful in using this ligand as an analytical reagent for estimation of metal ion.

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