

## 1, 4, 7-Triazacyclononane and N, N', N''-trimethyl-1, 4, 7-triazacyclononane – two versatile macrocycles for the synthesis of monomeric and oligomeric metal complexes

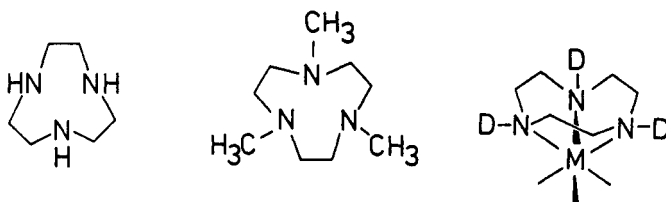
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**Abstract.** The tridentate, saturated macrocyclic ligand 1,4,7-triazacyclononane (L) forms stable pseudo-octahedral 2:1 complexes,  $ML_2^{n+}$ , with a large number of main group and transition metals in various and in some instance unusual oxidation states. In contrast, N,N',N''-trimethyl-1,4,7-triazacyclononane (L') forms only 1:1 complexes,  $L'MX_n$  ( $n = 1, 2, 3$ ). In complexes of this type the macrocycles function as effective blocking group for three coordination sites of a given metal center. The reactivity of this center may then be exploited by its oxidation or reduction or, alternatively, the unidentate ligands X may be substituted or reactions occurring at the coordinated ligand X may be studied.  $LMX_3$  and  $L'MX_3$  complexes are useful starting materials for the syntheses of binuclear complexes,  $[LM(\text{bridge})_nML]$ , containing a variety of bridging groups ( $O^{2-}$ ,  $OH^-$ ,  $N_3^-$ ,  $NCS^-$ ,  $[CrO_4]^{2-}$ ,  $[MoO_4]^{2-}$ ,  $R-CO_2^-$ ). In cases where M represents a paramagnetic transition metal center intramolecular spin exchange coupling phenomena are readily studied. The formation of oxo/hydroxo complexes of higher nuclearity (2-8) on hydrolysis of mononuclear  $LMX_3$  complexes has been observed:  $[(9\text{aneN}_3)_4M_4O_6]^{4+}$  ( $M = Ti(IV), Mn(IV)$ )  $[(9\text{aneN}_3)_6Fe_8(\mu-O)_2(\mu-OH)_{12}]^{8+}$ ,  $[(9\text{aneN}_3)_3Cr_3(OH)_5]^{4+}$ . Some of these species serve as model compounds for the active sites in metalloproteins which contain two or more metal ions per subunit.

### INTRODUCTION

The saturated macrocycles 1,4,7-triazacyclononane (L;  $[9\text{aneN}_3]$ ) (ref.1) and its N-methylated derivative N,N',N''-trimethyl-1,4,7-triazacyclononane (L',  $Me_3[9\text{aneN}_3]$ ) (ref. 2) are members of a family of potentially tridentate macrocyclic ligands which form thermodynamically and kinetically stable complexes with the heavier main group elements (Ga, In, Tl, Pb) and almost all transition metals (ref. 3). These cyclononane ligands occupy facially three coordination sites of an octahedron forming three stable five-membered rings,  $\overline{M-N-C-C-N}$ , adopting thereby a relatively rigid ( $\lambda\lambda\lambda$ )- (or  $(\delta\delta\delta)$ ) conformation. This stereochemical rigidity and the high symmetry of coordinated cyclononane ligands leads in general to very good crystallization behavior of complexes. These advantages of thermodynamic and kinetic stability, stereochemical rigidity and excellent crystallization of complexes is usually lost on going to tridentate macrocycles of larger ring sizes.



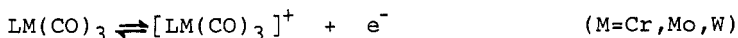
From the point of view of a synthetically orientated coordination chemist 1:1 complexes of the type  $[LMX_3]^n$  are of interest, where L represents one of the cyclononane macrocycles and X is a unidentate ligand of one kind or other. The macrocycle functions as an effective blocking group for three coordination sites and a series of chemical reactions (i) at the metal center (oxidation, reduction), (ii) substitution of X or (iii) reactions at X may be carried out without interference of ligand dissociation of L. In the present article such chemistry of the earlier transition metals (Ti, V, Cr, Mn, Fe, Mo, W, Re) will be emphasized since the coordination of N-donor macrocycles to these elements has in the past not been as extensively studied as the corresponding chemistry of Co(II,III), Ni(II) or Cu(II).

In addition, it will be shown that  $LMX_3$  complexes are excellent starting materials for the synthesis of binuclear and oligomeric complexes containing oxo- and/or hydroxo bridges as well as a variety of other bridging ligands.

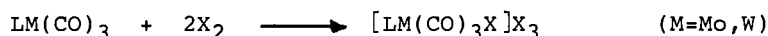
#### MONONUCLEAR 1:1 COMPLEXES OF Cr, Mo, W

The binding of N-donor macrocycles to inert metal centers such as chromium (III) or molybdenum and tungsten in oxidation states III to VI is usually slow and quite drastic reaction conditions are often required, which diminishes in many cases the yields.

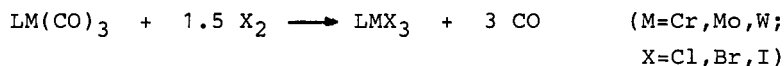
On the other hand, we have found that refluxing a solution of the respective hexacarbonylmetal(O) ( $M = Cr, Mo, W$ ) in decaline with the macrocycles  $[9]aneN_3$  or  $Me_3[9]aneN_3$  affords essentially quantitatively the colorless to yellow crystalline complexes  $([9]aneN_3)M(CO)_3$  or  $(Me_3[9]aneN_3)M(CO)_3$  (ref. 4-7). These materials proved to be very versatile starting complexes for a large variety of mononuclear and polynuclear species of chromium, molybdenum and tungsten in various oxidation states (III, IV, V and VI). These tricarbonyl(amine)-complexes are air-stable  $18e^-$ -species which in noncoordinating solvents such as  $CH_2Cl_2$  are reversible electrochemically oxidized to yield the cationic  $17e^-$ -species  $[LM(CO)_3]^+$  (ref. 5). The designation L will be used throughout this article if both macrocycles  $[9]aneN_3$  and  $Me_3[9]aneN_3$  are optional.



In the presence of halide ions (Cl, Br, I) the molybdenum and tungsten complexes are electrochemically oxidized to give the seven-coordinate complexes  $[LM(CO)_3X]^+$ . This reaction may also be achieved chemically via the reaction of the tricarbonyl complexes with  $Cl_2$ ,  $Br_2$ ,  $I_2$  in methylenechloride (ref. 4,5).



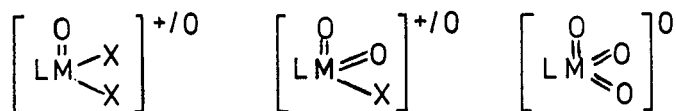
Using slightly more drastic reaction conditions (prolonged reaction times at higher temperatures) it is possible to exhaustively oxidatively decarbonylate the tricarbonyl-triazamacrocycle complexes of chromium, molybdenum and tungsten (ref. 5,8).



This reaction yields stable neutral, octahedral trihalogeno-complexes of Cr(III) and Mo(III) which are also accessible by substitution reactions of for instance  $\text{MX}_3(\text{thf})_3$  or  $[\text{MoCl}_5(\text{H}_2\text{O})]^{2-}$  complexes and the respective macrocycle but in lower yields (ref. 9).

$\text{LMX}_3$  complexes (Mo, W) are electrochemically reversibly oxidized yielding  $[\text{LMX}_3]^+$  cations where the metal centers are in the oxidation state +IV.  $(\text{Me}_3[9]\text{aneN}_3)\text{Mo}^{\text{III}}(\text{NCS})_3$  is electrochemically reversibly reduced to  $[(\text{Me}_3[9]\text{aneN}_3)\text{Mo}^{\text{II}}(\text{NCS})_3]^-$  and at more positive potentials oxidized to  $[(\text{Me}_3[9]\text{aneN}_3)\text{Mo}^{\text{IV}}(\text{NCS})_3]^+$  (ref. 5).

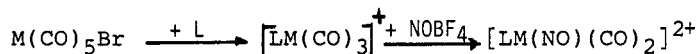
Using more drastic oxidative reaction conditions it is also possible to prepare a series of monomeric oxo-molybdenum and oxotungsten complexes from the tricarbonyl-triazamacrocycle-metal(O) complexes (ref. 5,6,8).



M=Mo, W; X=Cl, Br

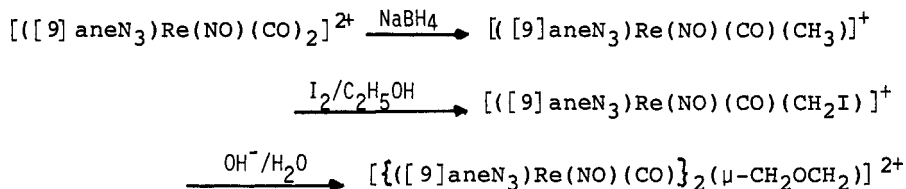
Quite fascinating is the oxidative decarbonylation reaction of  $\text{LM}(\text{CO})_3$  with 30%  $\text{H}_2\text{O}_2$  which yields essentially quantitatively the  $\text{LM}^{\text{VI}}\text{O}_3$  complexes (ref. 10). Thus the oxidation state of the metal center may be changed by six(!) units without any appreciable ligand dissociation interfering.

The chemistry described so far for Cr, Mo, and W has also been carried out with manganese and rhenium. Thus the reaction of  $[(\text{CO})_5\text{MBr}]$  (M=Mn, Re) with the tridentate macrocycles yields the cations  $[\text{LM}(\text{CO})_3]^+$  which are readily converted to nitrosyldicarbonyl complexes with use of  $\text{NOBF}_4$  (ref. 11).



$[(9)\text{aneN}_3]\text{Re}(\text{NO})(\text{CO})_2^{2+}$  is air-stable and water soluble; it reacts in  $\text{H}_2\text{O}$  with  $\text{Na}[\text{BH}_4]$  affording the air- and moisture-stable methyl complex

$[[9]aneN_3)Re(NO)(CO)(CH_3)]^+$  which was found to react with  $I_2$  (1:1) in absolute ethanol to give  $[[9]aneN_3)Re(NO)(CO)(CH_2I)]^+$  which slowly



dimerizes in aqueous solution to produce an organometallic dication with a bridging 2-oxa-propane-1,3-diyl group (ref. 12,13). The structure of this complex is shown in Figure 1.

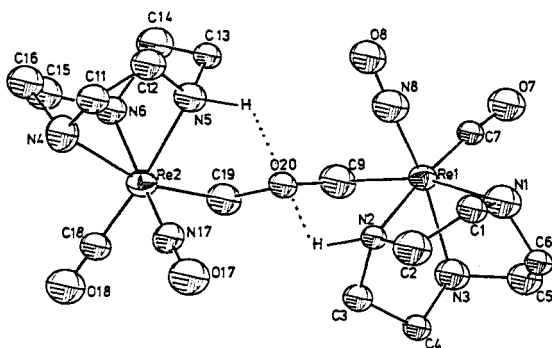


Fig.1: The structure of  $[\{LRe(NO)(CO)\}_2(CH_2OCH_2)]^{2+}$  indicating the intramolecular N-H...O hydrogen bonds

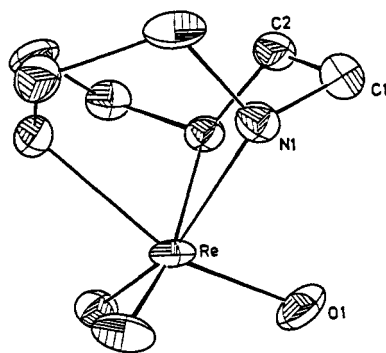
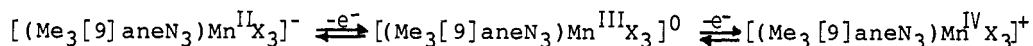


Fig.2: The structure of  $[LReO_3]^+$

Interestingly, the oxygen atom of the  $CH_2-O-CH_2$ -bridge is hydrogen bonded to one N-H group of each coordinated triazacyclononane ligand. Thus two N-H...O bonds are formed (ref. 13).

$[[9]aneN_3)Re(NO)(CO)_2]^{2+}$  reacts with 30%  $H_2O_2$  to yield quantitatively  $[[9]aneN_3)ReO_3]^+$  the structure of which is shown in Figure 2. Again the change of oxidation states of six units at the metal center does not lead to appreciable ligand dissociation during the redox reaction (ref. 11).

A series of complexes  $(Me_3[9]aneN_3)Mn^{II}X_3$  where X represents  $Cl^-$ ,  $Br^-$ ,  $N_3^-$  or  $NCS^-$  is soluble in acetonitrile and cyclic voltammetry establishes that the oxidation states II, III and IV of these monomers are reversibly accessible (ref. 14).



Monomeric complexes  $LMX_3$  (M = Ga, In, Ti, V, Cr, Mn, Fe, Co; X = Cl, Br,  $H_2O$ ) have been prepared via reaction of the trichlorides or aqua metal perchlorates with both macrocycles; they are starting materials for the synthesis of binuclear and oligomeric complexes.



Figures 3 and 4 show their structures. Note the subtle difference between the  $\text{NiN}_6$ -polyhedron and the  $\text{CuN}_5$ -polyhedron (or  $\text{CuN}_6$  if the long  $\text{Cu-N}_\gamma$  distance is considered a  $\text{Cu-N}$  bond). In both complexes intramolecular antiferromagnetic spin exchange coupling is observed ( $H = -2JS_1S_2$ ;  $J$  for the  $\text{Ni}_2$ :  $-71 \text{ cm}^{-1}$ , and  $J = -331 \text{ cm}^{-1}$  for the  $\text{Cu(II)}_2$ ).

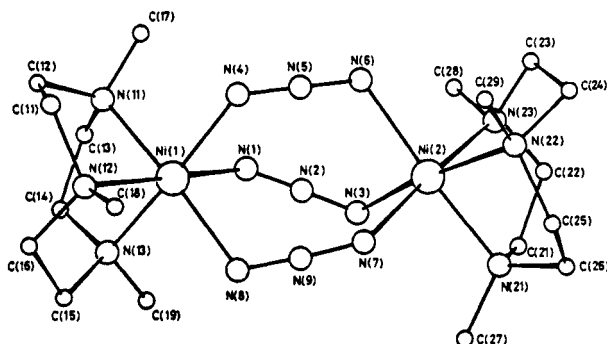


Fig. 3: Structure of  $[\text{L}_2\text{Ni}_2(\mu\text{-N}_3)_3]^+$

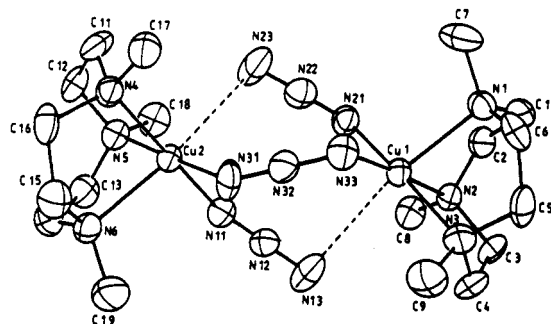


Fig. 4: Structure of  $[\text{L}_2\text{Cu}_2(\mu\text{-N}_3)_3]^+$

A series of binuclear complexes containing the  $\mu$ -oxo-di- $\mu$ -carboxylato-dimetal core of iron(III), manganese(III) and vanadium(III) have been prepared via spontaneous self-assembly from mononuclear starting materials ( $[\text{9}] \text{aneN}_3$ ) $\text{MCl}_3$ , ( $\text{Me}_3[\text{9}] \text{aneN}_3$ ) $\text{MCl}_3$ , and  $\text{Mn}(\text{ac})_3$  (ref. 25,26,27,28). From a methanolic solution of  $\text{Me}_3[\text{9}] \text{aneN}_3$ ,  $\text{Fe}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Na}$ -acetate the hydroxo-bridged dimer  $[\text{L}_2\text{Fe}_2(\mu\text{-OH})(\mu\text{-CH}_2\text{CO}_2)_2]^+$  has been isolated as yellow, air-sensitive crystals (ref. 26, 29). Figure 5 shows the structure of the iron(III)-dimer and Figure 6 that of the iron(II)-dimer. These binuclear units have been identified in some metalloproteins e.g. hemerythrin ( $\text{Fe}^{\text{III}}$ ), deoxyhemerythrin ( $\text{Fe}^{\text{II}}$ ) and a pseudo-catalase isolated from *Lactobacillus plantarum* ( $\text{Mn}$ ). The above complexes are considered to be useful low molecular weight models for the active sites of these biomolecules. This is a further fruitful area where macrocyclic  $\text{N}$ -donor ligands play an important role. They mimic the binding of transition metals to the protein and resemble in this respect the widely used hydro-tris-(pyrazolyl)borates (ref. 30).

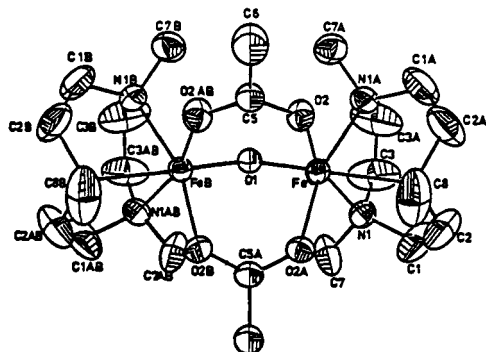


Fig. 5: The structure of  $[(\text{Me}_3[\text{9}] \text{aneN}_3)_2\text{Fe}_2(\mu\text{-O})(\mu\text{-CH}_3\text{CO}_2)_2]^+$  (ref. 26,29)

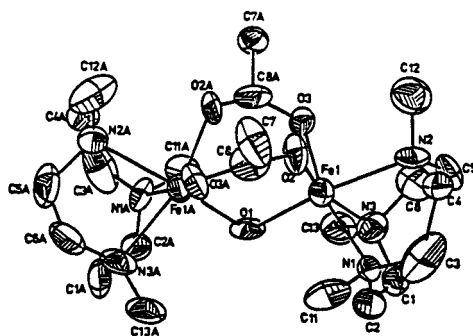


Fig. 6: The structure of  $[(\text{Me}_3[\text{9}] \text{aneN}_3)_2\text{Fe}_2(\mu\text{-OH})(\mu\text{-CH}_3\text{CO}_2)_2]^+$  (ref. 26,29)

Finally, Chaudhuri has recently shown that  $[\text{CrO}_4]^{2-}$ ,  $[\text{MoO}_4]^{2-}$  may act as bridge between two  $(\text{Me}_3[9]\text{aneN}_3)\text{Fe}^{\text{III}}$  moieties. Thus the neutral complexes  $[(\text{Me}_3[9]\text{aneN}_3)_2\text{Fe}_2(\mu\text{-XO}_4)_3]$  have been prepared ( $X = \text{Cr, Mo, W}$ ) (ref. 31); the structure of the chromate derivative is shown in Figure 7.

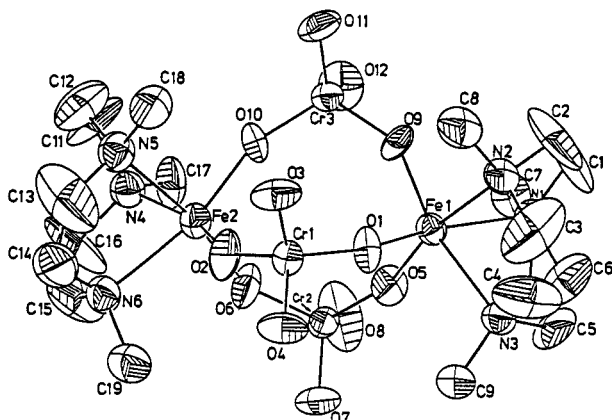


Fig. 7: The structure of  $[(\text{Me}_3[9]\text{aneN}_3)_2\text{Fe}_2(\mu\text{-CrO}_4)_3]$

The condensation reaction of monomeric  $[(9]\text{aneN}_3)\text{Cr}(\text{OH}_2)_3]^{3+}$  in aqueous solution yields the trimeric cation  $[(9)\text{aneN}_3)_3\text{Cr}_3(\mu\text{-OH})_4(\text{OH})]^{4+}$  and not the expected tri- $\mu$ -hydroxo bridged dimer (ref. 16). For molybdenum(IV) and tungsten(IV) trimeric species  $[(9)\text{aneN}_3)_3\text{W}_3\text{O}_4]^{4+}$  (ref.6) and  $[(9)\text{aneN}_3)_3\text{Mo}_3\text{S}_4]^{4+}$  (ref.32) have been synthesized. These complexes contain the well-known triangular  $\{\text{M}_3\text{X}_4\}^{4+}$  unit ( $\text{M}=\text{Mo, W}$ ;  $\text{X}=\text{O, S}$ ), where each metal center is coordinated to one tridentate  $[9]\text{aneN}_3$  ligand. A further condensation reaction of  $([9]\text{aneN}_3)\text{M}^{\text{III}}$ - or  $([9]\text{aneN}_3)\text{M}^{\text{IV}}$ -units leading to tetrameric cations of the type  $[(9)\text{aneN}_3)_4\text{M}_4\text{O}_6]^{4+}$  ( $\text{M}=\text{Ti}^{\text{IV}}, \text{Mn}^{\text{IV}}$ ) (ref.34,33) and  $[(9)\text{aneN}_3)_4\text{M}_4(\text{OH})_6]^{6+}$  ( $\text{M}=\text{In}^{\text{III}}$ ) (ref.35) has been found. It appears that this adamantane-like  $[\text{M}_4^{\text{IV}}\text{O}_6]^{4+}$  or  $[\text{M}_4^{\text{III}}(\text{OH})_6]^{6+}$  skeleton is a quite stable condensation product of four  $[\text{LM}(\text{OH}_2)_3]^{\text{III}}$  complexes, where each metal center is in a distorted octahedral  $\text{N}_3\text{O}_3$  donor set.

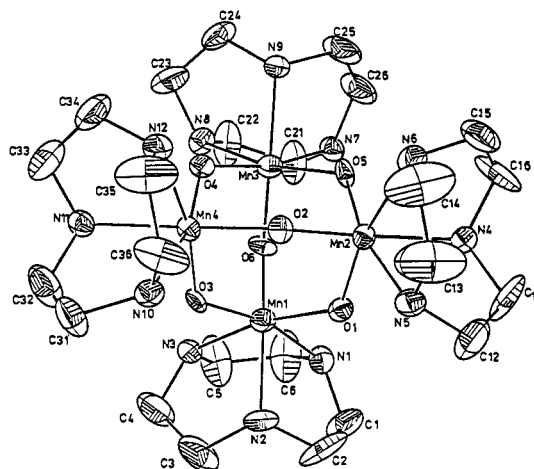


Fig.8: The structure of  $[(9)\text{aneN}_3)_4\text{Mn}_4\text{O}_6]^{4+}$

Hydrolysis of  $([9]\text{aneN}_3)\text{FeCl}_3$  in aqueous solution (pH 8-9) and addition of sodium bromide affords quantitatively  $[(9)\text{aneN}_3)_6\text{Fe}_8(\mu\text{-O})_2(\mu\text{-OH})_{12}]\text{Br}_8 \cdot 9\text{H}_2\text{O}$  - an octameric cation of iron(III) (ref.36). Six  $\text{Fe}^{\text{III}}$  centers have an octahedral  $\text{fac-N}_3\text{O}_3$ -donor set whereas the remaining two  $\text{Fe}^{\text{III}}$  are in an octahedral oxygen atom environment. Seven bromide ions are attached to the surface of the octameric cation via  $\text{N-H}\cdots\text{Br}$  and  $\text{O-H}\cdots\text{Br}$  hydrogen bonding yielding a monocation  $[\text{L}_6\text{Fe}_8(\mu\text{-O})_3(\mu\text{-OH})_{12}\text{Br}_7\text{H}_2\text{O}]^+$  and an isolated  $[\text{Br} \cdot 8\text{H}_2\text{O}]^-$  anion.

Recently, Chaudhuri et al. (ref. 31) have shown that it is possible to quantitatively generate cationic heteropolyoxo-molybdenum(VI) or tungsten (VI) complexes of the composition  $[(Me_3[9]aneN_3)_3Fe_3Mo_4O_{14}(\mu-OCH_3)_3]^{2+}$  and  $[(Me_3[9]aneN_3)_3Fe_3W_4O_{14}(\mu-OCH_3)_3]^{2+}$ . This opens up a new field of heteropolyoxometalate chemistry.

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