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, $LMX_n$ (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 $LMX_3$ complexes are useful starting materials for the syntheses of binuclear complexes, $[LM(bridge)MN]$, containing a variety of bridging groups ($O_2^-$, $O^-\text{H}_2$, $N_3^-$, $NCS^-\text{[Cr}O_4^2^-\text{]}$, $[\text{M}O_4^2^-; R-CO_2^-]$). 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: $[(\text{[9}aneN_3]_4\text{M}O_6)_4^{4+}$ (M = Ti(IV), Mn(IV)) $[(\text{[9}aneN_3]_2\text{C}F_8(\mu-O)_2^2^2^2^2^2^2^2^2^2^2^2^2^2^2 (\mu-OH)_2]$ $[\text{(9}aneN_3]_3\text{Cr}_3(\text{OH})_5]^4+$. 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]aneN₃) (ref. 1) and its N-methylated derivative N,N',N''-trimethyl-1,4,7-triazacyclononane (L', Me₃[9]ane N₃) (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, $\text{N-\text{C}-\text{C}-\text{N}}$, adopting thereby a relatively rigid (\text{\lambda\lambda\lambda})- (or (\text{\lambda\lambda\lambda})- (or (\text{\lambda\lambda\lambda})-) 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(0) \((M = Cr, Mo, W)\) 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 CHCl\(_3\) 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.

\[
LM(CO)_3 \rightleftharpoons [LM(CO)_3]^+ + e^- \quad (M = Cr, Mo, W)
\]

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 methylene chloride (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).

\[
LM(CO)_3 + 2X_2 \rightarrow [LM(CO)_3X]_3 \quad (M=Mo,W)
\]

This reaction yields stable neutral, octahedral trihalogeno-complexes of Cr(III) and Mo(III) which are also accessible by substitution reactions of for instance MX₃(thf)₃ or [MoCl₅(H₂O)]²⁻ complexes and the respective macrocycle but in lower yields (ref. 9).

LMX₃ complexes (Mo, W) are electrochemically reversibly oxidized yielding [LMX₃]⁺ cations where the metal centers are in the oxidation state +IV. [(Me₃[9]aneN₃)Mo]ᴵᴵ⁺(NCS)₃ is electrochemically reversibly reduced to [(Me₃[9]aneN₃)Mo]ᴵ⁺(NCS)₃⁻ and at more positive potentials oxidized to [(Me₃[9]aneN₃)Mo]⁴⁺(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(0) complexes (ref. 5,6,8).

Quite fascinating is the oxidative decarbonylation reaction of LM(CO)₃ with 30% H₂O₂ which yields essentially quantitatively the LMVIO₃ 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 [(CO)₅MBr] (M=Mn,Re) with the tridentate macrocycles yields the cations [LM(CO)₃]⁺ which are readily converted to nitrosyl dicarbonyl complexes with use of NOBF₄ (ref. 11).

\[
M(CO)₅Br + NOBF₄ \rightarrow [LM(CO)₃]⁺ + NOBF₄ \rightarrow [LM(NO)(CO)₂]^{2+}
\]

\([(9)aneN₃]Re(NO)(CO)₂]^{2+}\) is air-stable and water soluble; it reacts in H₂O with Na[BH₄] affording the air- and moisture-stable methylcomplex.
[(9)aneN3]Re(NO)(CO) (CH3)2+ which was found to react with I2 (1:1) in absolute ethanol to give [([(9)aneN3]Re(NO)(CO)(CH2I))2]2+ which slowly dimerizes in aqueous solution to produce an organometallic dication with a bridging 2-oxa-propane-1,3-diy1 group (ref. 12,13). The structure of this complex is shown in Figure 1.

Interestingly, the oxygen atom of the CH2-O-CH2-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)aneN3]Re(NO)(CO)22+ reacts with 30% H2O2 to yield quantitatively [(9)aneN3]ReO3+ 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 (Me3 [9]aneN3)MnIII X3 where X represents Cl-, Br-, N3- 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 LMX3 (M = Ga, In, Ti, V, Cr, Mn, Fe, Co; X = Cl, Br, H2O) 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.
BINUCLEAR AND POLYNUCLEAR COMPLEXES

Hydrolysis of monomeric \([\{([9\text{ane}\text{N}_3\text{]}^\text{III}]\text{M}^{\text{III}}\text{X}_3\text{]}^{\text{n}+}\) or \([\{\text{Me}_3[9\text{ane}\text{N}_3\text{]}\text{M}^{\text{III}}\text{X}_3\text{]}^{\text{n}+}\) species in aqueous solution (pH 8-9) where M is a trivalent metal such as Ga\text{III} (ref. 15), Cr\text{III} (ref. 16), Co\text{III} (ref. 17) and Rh\text{III} (ref. 18) and X = Cl, Br or H\text{2O} yields in the absence of other coordinating anions tris-\(\mu\)-hydroxo and/or di-\(\mu\)-hydroxo bridged dimers, which are in some instances - depending on the pH of the solution - interconvertible.

\[
\left[\begin{array}{c}
\text{L} \\
\text{M} \\
\text{H}_2\text{O} \\
\text{L}
\end{array}\right]^{\text{3+}} + \text{H}_2\text{O} \rightleftharpoons \left[\begin{array}{c}
\text{L} \\
\text{M} \\
\text{H}_2\text{O} \\
\text{L}
\end{array}\right]^{\text{2+}} + 2\text{H}^{\text{+}} \rightleftharpoons \left[\begin{array}{c}
\text{H}_2\text{O} \\
\text{L} \\
\text{M} \\
\text{L}
\end{array}\right]^{\text{6+}}
\]

In cases where L represents Me\text{3}[9\text{ane}\text{N}_3\text{]} the conversion of two face-sharing octahedra in the tri-\(\mu\)-hydroxo bridged species into two edge-sharing octahedra of the di-\(\mu\)-hydroxo-bridged complex is not feasible due to steric constraints of the N-CH\text{3} group of one amine ligand with the terminal OH- (or H\text{2O}) group at the other metal center and vice versa (ref. 2).

Hydrolysis of \([\{[9\text{ane}\text{N}_3\]}\text{MoCl}_3\) affords green, extremely air-sensitive di-\(\mu\)-hydroxo-bridged dimers which contain strong metal-metal bonds of the bond order three (\(\sigma^2\pi^4\)) (ref. 19). Oxidation of these species with O\text{2} or Cl\text{O}_2 yields quantitatively di-\(\mu\)-oxo-dimolybdenum(V) dimers with a metal-metal bond order of one (ref. 9, 20).

\[
\left[\begin{array}{c}
\text{X} \\
\text{L} \\
\text{M}_\text{O} \\
\text{L} \text{O} \text{X}
\end{array}\right]^{\text{n+}} \text{O}_2 \text{ or ClO}_2^- \rightarrow \left[\begin{array}{c}
\text{O} \\
\text{L} \\
\text{M}_\text{O} \\
\text{L} \text{O} \text{L}
\end{array}\right]^{\text{2+}} \text{H}^{\text{+}} \rightarrow \left[\begin{array}{c}
\text{O} \\
\text{L} \\
\text{M}_\text{O} \\
\text{L} \text{O} \text{L}
\end{array}\right]^{\text{2+}}
\]

If these hydrolysis reactions are carried out in the presence of acetate or carbonate ions, di-\(\mu\)-hydroxo-\(\mu\)-acetato or di-\(\mu\)-hydroxo-\(\mu\)-carbonato binuclear complexes are formed.

The Mo(III)\text{2}-dimer contains a metal-metal triple bond (Mo-Mo 2.471(2) \(\AA\); ref. 19); for the Ru(III)\text{2} dimer a Ru-Ru single bond has been observed (Ru-Ru 2.572(3) \(\AA\); ref. 21) whereas in the Cr(III)\text{2} complex the Cr...Cr distance of 2.898(2) \(\AA\) (ref. 22) indicates the absence of a direct metal-metal bond.

It is also possible to introduce other bridging ligands such as N\text{3} or NCS\text{2}:\text{2} For example, \([\{\text{Me}_3[9\text{ane}\text{N}_3\text{]}\text{Cu(OH}_2\text{)}_2\text{]}^{\text{2+}}\) and \([\{\text{Me}_3[9\text{ane}\text{N}_3\text{]}\text{Ni(OH}_2\text{)}_3\text{]}^{\text{2+}}\) react in methanol with NaN\text{3} to form the binuclear complexes \([\{\text{Me}_3[9\text{ane}\text{N}_3\text{]}\text{2N}_2(\mu-N_3)_3\text{]}^{\text{2+}}\text{ (M = Cu}^{\text{II}}, \text{Ni}^{\text{II}}\text{) (ref. 23, 24).}
Figures 3 and 4 show their structures. Note the subtle difference between the NiN$_6$-polyhedron and the CuN$_5$-polyhedron (or CuN$_6$ if the long Cu-N$_\infty$ distance is considered a Cu-N bond). In both complexes intramolecular antiferromagnetic spin exchange coupling is observed ($H = -2JS_1S_2$; $J$ for the Ni$_2$: $-71$ cm$^{-1}$, and $J = -331$ cm$^{-1}$ for the Cu(II)$_2$).

A series of binuclear complexes containing the $\mu$-oxo-$\mu$-carboxylato-dimetal core of iron(III), manganese(III) and vanadium(II) have been prepared via spontaneous self-assembly from mononuclear starting materials ([9]aneN$_3$)MC$_3$, (Me$_3$[9]aneN$_3$)MC$_3$, and Mn(ac)$_3$ (ref. 25, 26, 27, 28). From a methanolic solution of Me$_3$[9]aneN$_3$, Fe(CIO$_4$)$_2$·6H$_2$O and Na-acetate the hydroxo-bridged dimer [L$_2$Fe$_2$(μ-OH)(μ-CH$_2$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 (Fe$^{II}$), deoxyhemerythrin (Fe$^{II}$) and a pseudo-catalase isolated from Lactobacillus plantarum (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 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).
Finally, Chaudhuri has recently shown that \([\text{CrO}_4]^{2-},[\text{MoO}_4]^{2-}\) may act as bridge between two \((\text{Me}_3[9]\text{aneN}_3)\text{Fe}^{III}\) moieties. Thus the neutral complexes \((\text{Me}_3[9]\text{aneN}_3)\text{Fe}_2(\mu-\text{XC}_4)_3\) have been prepared \((X = \text{Cr}, \text{Mo}, \text{W})\) (ref. 31); the structure of the chromate derivative is shown in Figure 7.

The condensation reaction of monomeric \(\left[[9]\text{aneN}_3\right]\text{Cr(OH}_2)_3]^{3+}\) in aqueous solution yields the trimeric cation \(\left[[9]\text{aneN}_3\right]_3\text{Cr}_3(\mu-OH)_4(OH)_3\right]^{4+}\) and not the expected tri-\(\mu\)-hydroxo bridged dimer (ref. 16). For molybdenum(IV) and tungsten(IV) trimeric species \(\left[[9]\text{aneN}_3\right]_3\text{M}_3\text{O}_4\right]^{4+}\) (ref. 6) and \(\left[[9]\text{aneN}_3\right]_3\text{Mo}_3\text{S}_4\right]^{4+}\) (ref. 32) have been synthesized. These complexes contain the well-known triangular \(\left[M_3\text{X}_4\right]^{4+}\) unit \((M=\text{Mo}, \text{W}; X=\text{O}, \text{S})\), where each metal center is coordinated to one tridentate \([9]\text{aneN}_3\) ligand. A further condensation reaction of \(\left[[9]\text{aneN}_3\right]_4\text{M}_4\text{O}_6\right]^{4+}\) \((M=\text{Ti}^{IV}, \text{Mn}^{IV})\) (ref. 34, 33) and \(\left[[9]\text{aneN}_3\right]_4\text{M}_4(\text{OH})_6\right]^{6+}\) \((M=\text{In}^{III})\) (ref. 35) has been found. It appears that this adamantane-like \([M]^{IV}\text{O}_6\right]^{4+}\) or \([\text{M}^{III}(\text{OH})_6]^{6+}\) skeleton is a quite stable condensation product of four \([LM(\text{OH})_2]_3]^{3+}\) complexes, where each metal center is in a distorted octahedral \(N_3O_3\) donor set.

Hydrolysis of \(\left[[9]\text{ane N}_3\right]\text{FeCl}_3\) in aqueous solution \((\text{pH} 8-9)\) and addition of sodium bromide affords quantitatively \(\left[[9]\text{aneN}_3\right]_6\text{Fe}_8(\mu-O)_2(\mu-OH)_2\text{Br}_8\cdot 9\text{H}_2\text{O}\) - an octameric cation of iron(III) (ref. 36). Six \(\text{Fe}^{III}\) centers have an octahedral \(\mu-N_3O_3\)-donor set whereas the remaining two \(\text{Fe}^{III}\) are in an octahedral oxygen atom environment. Seven bromide ions are attached to the surface of the octameric cation via \(\text{N-H...Br}\) and \(\text{O-H...Br}\) hydrogen bonding yielding a monocation \([\text{L}_6\text{Fe}_8(\mu-O)_3(\mu-OH)_2\text{Br}_7\text{H}_2\text{O}^\cdot]^+\) and an isolated \([\text{Br\cdot8H}_2\text{O}^\cdot]^+\) 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 \[[\text{Me}_3[\text{9} \text{aneN}_3]_3\text{Fe}_3\text{M}_0_4\text{O}_{4} \text{O}_4(u-\text{OCH}_3)_3]^{2+}\] and \[[\text{Me}_3[\text{9} \text{aneN}_3]_3\text{Fe}_3\text{W}_4\text{O}_{4} \text{O}_4(u-\text{OCH}_3)_3]^{2+}\]. This opens up a new field of heteropolyoxometalate chemistry.

REFERENCES AND NOTES

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