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Review

Metallacycles derived from metal complexes of exo-coordinated macrocyclic ligands

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ABSTRACT

The assembly of metallacyclic structures incorporating exo-coordinated macrocyclic ligand components is reviewed. The exo-coordination approach provides a means for building extended cyclic assemblies and contrasts with the use of conventional endocyclic macrocyclic coordination which generally results in metal-in-cavity products. The approach, which depends on the availability of one or more donor atoms bearing electron lone pairs that are oriented exo to their macrocyclic cavity, has been employed to produce a range of diverse metallacyclic structures; examples of such metallo-assemblies displaying cyclic dimeric, trimeric, tetrameric, and hexameric topologies are presented.

1. Introduction

Synthetic macrocyclic ligand chemistry has now been investigated for more than five decades [1,2]. As well as studies aimed at modeling aspects of the behavior and properties of Nature's macrocycles, there have also been a large number of reports concerned with the design and synthesis of new macrocyclic ligands for applications involving the separation or sensing of metal ions.

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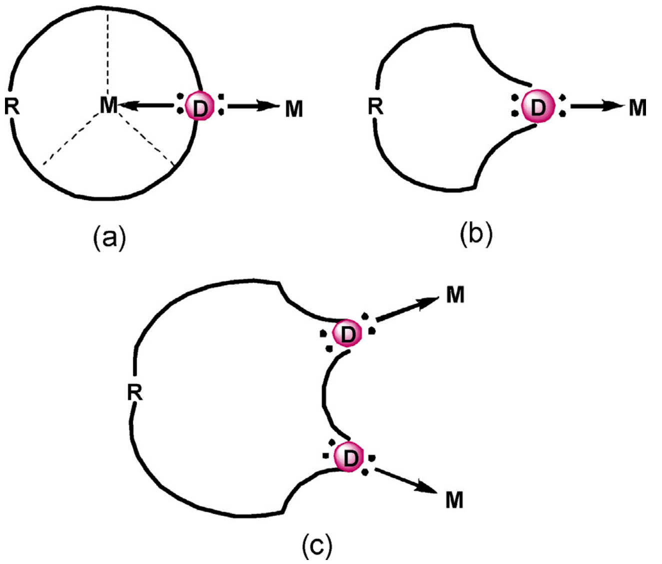


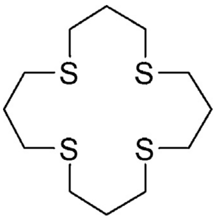
Fig. 1. Three representative exodentate donor atom bridging arrangements, where D is a thioether sulfur, an ether oxygen, or an amido nitrogen donor. In (a) D displays four connectivity involving both endo- and exo-directed donor coordination, whereas for (b) and (c) only exo-directed coordination and three connectivity are present. Use of a secondary or tertiary amine nitrogen for D in (b) and (c) may also give rise to corresponding exodentate coordination behavior.

Macrocyclic ligands have proved particularly suitable for applications of this latter type since their cyclic nature serves to both restrict the ring's conformational flexibility as well as providing a central cavity which, at least in principle, can be tailored to match both the steric and electronic requirements of a metal-ion of interest [3–8]. As a consequence, investigations of the above type have very commonly involved solely endo coordination – that is, binding of the metal ion in the macrocyclic cavity. Reports of macrocyclic systems in which exo- (or partial exo-) coordination are present are considerably less common [9]. Nevertheless, collectively the latter complexes represent an interesting and varied structural group comprising both discrete and coordination framework derivatives.

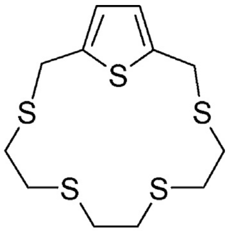
The structural diversity observed for the above group largely arises from the ability to connect the macrocyclic building blocks via metal centers using a variety of bridging arrangements [9]. In turn, this requires the presence of exo-oriented electron lone-pairs on particular macrocyclic donor atoms such that three or four atom connectivities occur for these donors on formation of the desired bridged metal species. This condition has most frequently been met by employing macrocyclic ring thioether, ether, amine or amido bridging groups, either singly or in combination, to link adjacent macrocyclic complex units; three representative exo-oriented donor atom bridging arrangements, in which each "D" is surrounded by a tetrahedral array of electron pairs (two lone and two bonding pairs), are illustrated schematically in Fig. 1.

Considerable progress has now been made in elucidating structure–function relationships within individual systems of the above type and the use of exo-coordination is clearly a synthetically attractive strategy for constructing new metallo-supramolecular entities based on macrocyclic ligand building blocks; although the rational synthesis of many such metallo-species still often remains a challenge.

A sub-category within the discrete systems mentioned above consists of metallacyclic systems comprised of bridged cyclic dimers, trimers, tetramers, and hexamers; cyclic entities of this type form the subject of the present review. No comprehensive review of such macrocycle-containing metallacyclic derivatives has been reported previously.



L^1



L^2

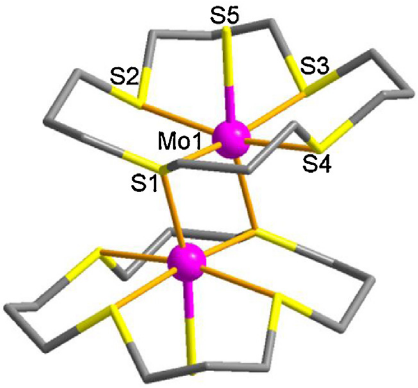


Fig. 2. X-ray structure of the doubly bridged dimer, $[Mo_2(\mathbf{L^1})_2(SH)_2](CF_3SO_3)_2{\cdot}2H_2O$ (**1**). Solvate water molecules are not shown [16].

2. Metallacyclic dimers

Dinuclear species of stoichiometry M_2L_2 incorporating a range of metal ions and a variety of macrocyclic ligands are the most commonly reported examples of discrete metallacycles of the present type, although an example of type M_2L_4 is also known (see later).

2.1. All thia donor macrocyclic systems

Thia donor macrocycles frequently show unusual coordination behavior toward softer metal ions and, for example, give rise to less-common coordination topologies [9]. This results from the well established propensity for macrocyclic ring thioether donors to promote exodentate coordination [10–13] – often generating bridged oligo- [14] or polymeric [15] metal coordination species. The origins of such behavior lie in the well documented tendency for thioether sulfur in macrocyclic rings to be associated with an *anti* torsional arrangement in the macrocyclic backbone (reflecting both steric and electrostatic effects) rather than the more usual *gauche* arrangement favored by an analogous atom sequence in which sulfur is replaced by oxygen or nitrogen.

In early studies two examples of doubly bridged dimers based on the S_4- and S_5-donor macrocycles, **L^1** and **L^2**, were reported [16,17]. The first of these is a dimolybenum(II) dimer with the unusual stoichiometry $[Mo_2(\mathbf{L^1})_2(SH)_2](CF_3SO_3)_2{\cdot}2H_2O$ (**1**). This product was shown by X-ray diffraction to have a doubly thia-bridged binuclear structure in which all S-donors of each **L^1** macrocycle bind to a metal center in an endo fashion (Fig. 2) [16]. One thioether donor from each metal bound macrocycle also bridges to the metal