Coordination Chemistry Reviews 280 (2014) 176–202

Contents lists available at ScienceDirect

Coordination Chemistry Reviews

journal homepage: www.elsevier.com/locate/ccr

Review

Recent developments in the thiamacrocyclic chemistry of the latter d-block elements

Seulgi Kim [a], Leonard F. Lindoy [a,b,*], Shim Sung Lee [a,**]

[a] *Department of Chemistry and Research Institute of Natural Science, Gyeongsang National University, Jinju 660-701, South Korea*
[b] *School of Chemistry, F11, The University of Sydney, Sydney 2006, NSW, Australia*

Contents

ARTICLE INFO

Article history:
Received 21 July 2014
Accepted 22 August 2014
Available online 1 September 2014

Keywords:
Macrocycle
Sulfur donor
Thiacrown
Thiamacrocycle
Endocyclic and exocyclic coordination
Coordination polymer

ABSTRACT

In this review we present the metal complexation chemistry of sulfur donor macrocyclic ligands since 2006, including mixed sulfur, nitrogen and/or oxygen systems with the latter d-block metal ions. Both discrete and polymeric systems are discussed.

1. Introduction

Synthetic macrocyclic ligands have long been investigated as selective metal-ion binding reagents [1–4]. The suitability of macrocycles for this role arises from their cyclic nature which provides a 'preformed' receptor cavity as the metal binding site. The restricted conformational flexibility associated with the macrocyclic ring also assists in matching the cavity size of the macrocycle to the steric (and electronic) requirements of the metal ion of interest [5,6]. As such, macrocycles have formed the basis for a range of applications, especially involving the sensing and/or separation of various substrates [7–16]. Macrocyclic ligand complexes also characteristically show enhanced kinetic and thermodynamic stabilities over their open-chain analogues (the macrocycle effect) [2] and this has also resulted in them being attractive for use in a number of applications [17–20], including their use as robust building blocks for the assembly of supramolecular architectures [21,22]. In the above cases the metal ion typically displays endo (in cavity) complexation [Fig. 1(a)]. Although less common, there are now also a considerable number of examples of macrocyclic systems that exhibit metal ion binding exo to their macrocyclic cavities [Fig. 1(b)] [23]. Exo-coordination is quite commonly associated with (but not restricted to) [24,25] thioether-containing macrocycles, reflecting the tendency for this donor type to be oriented exo

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* Corresponding author at: School of Chemistry, F11, The University of Sydney, Sydney, NSW 2006, Australia.
** Corresponding author at: Department of Chemistry and Research Institute of Natural Science, Gyeongsang National University, Jinju 660-701, South Korea.
E-mail addresses: L.Lindoy@chem.usyd.edu.au (L.F. Lindoy), sslee@gnu.ac.kr (S.S. Lee).

http://dx.doi.org/10.1016/j.ccr.2014.08.011
0010-8545/

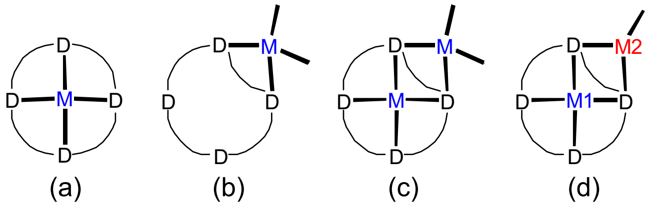


Fig. 1. Schematic representation of (a) endocyclic, (b) exocyclic, (c) homonuclear endo/exocyclic and (d) heteronuclear endo/exocyclic coordination.

with respect to the metal free macrocyclic cavity [26–29]. Studies of this type have very often employed a soft metal ion such as silver(I) or copper(I) because of their well documented affinity for soft sulfur donors. Further, d^{10} metal ions such as these are free of crystal field influences and hence readily adopt variable coordination numbers and/or geometries—behaviour that may allow the generation of unusual (often irregular) structures.

A smaller number of macrocyclic systems have been prepared incorporating ring systems that simultaneously display both endo- and exocyclic coordination to yield product structures that uniquely reflect the presence of dual coordination modes; both homo- and heteronuclear endo/exo systems have been reported [Fig. 1(c) and (d)].

In this review the latter d-block metal ion chemistry of macrocyclic ligands incorporating sulfur donors, including mixed sulfur, nitrogen and/or oxygen donor systems is presented. Supramolecular aspects as well as structure-function relationships involving such metal complex systems are discussed. Exocyclic thiamacrocycle coordination of a range of metal ions leading to the generation of discrete metallacycles as well as to framework materials has been the subject of recent reviews from the authors' group [23,30]. Both exo and endo systems are included in the present discussion, however, in general, only exo systems not covered in these previous reviews are presented. The present discussion is aimed at being complementary to these above reviews.

Overall, the coverage of the present review is restricted to the more recent work (since 2006). A chapter focused on organic synthetic procedures for obtaining 10-membered or larger macrocycles incorporating one or more S-atoms was published in 2008; this report includes a tabulation of corresponding thia-macrocyclic metal complexes covering the literature up to early 2007 [31]. A perspective review describing mixed-ligand pnictogen/thiacrown complexes of palladium(II) and platinum(II) appeared in 2012 [32]; only representative recent examples of the latter complexes are included in the present work. Systems involving thia derivatives of porphyrins and calixarenes fall outside the present scope and are not discussed.

A range of studies involving the use of thia-containing macrocycles as the metal ion recognition site in fluorescent sensors have now been reported—only selected examples of such systems are presented in the present discussion. Similarly, there are a number cases of thia-containing macrocycles employed as ionophores in metal ion solvent extraction and membrane transport experiments in the absence of parallel studies on the mode of metal coordination involved. Studies of this type are excluded from the discussion.

2. All thia donor ring systems

X-ray structures of the bis-ligand cadmium(II) complexes of 1,4,7-trithiacyclononane ($\mathbf{L}^1$) and 1,4,7,10-tetrathiacyclododecane ($\mathbf{L}^2$) of type $[\mathrm{Cd(L)_2}](\mathrm{ClO_4})_2$ were reported as part of an investigation aimed at relating the ^{113}Cd NMR shift behaviour to the respective complex structures [33].

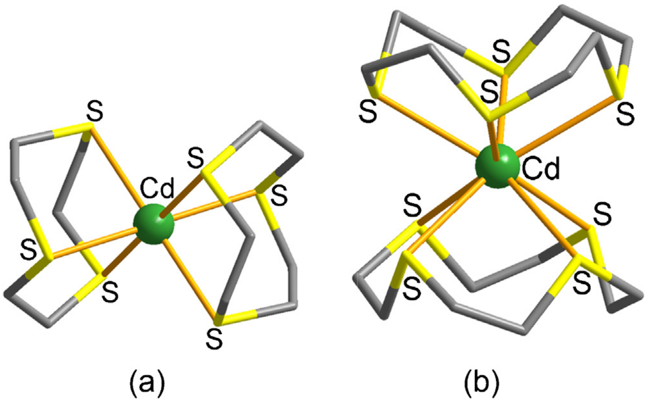
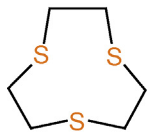
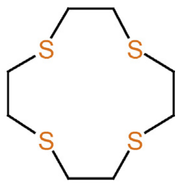


Fig. 2. X-ray structures of (a) $[\mathrm{Cd}(\mathbf{L}^1)_2](\mathrm{PF_6})_2$ (**1**) and (b) $[\mathrm{Cd}(\mathbf{L}^2)_2](\mathrm{ClO_4})_2$ (**2**). Non-coordinating anions are not shown [34].



$\mathbf{L^1}$



$\mathbf{L^2}$

In $[\mathrm{Cd}(\mathbf{L}^1)_2](\mathrm{PF_6})_2$ (**1**) [Fig. 2(a)], the two $\mathbf{L}^1$ ligands bind facially via their three sulfur atoms to give a distorted octahedral coordination geometry—a common structural arrangement found in other bis-ligand metal complexes of $\mathbf{L}^1$ [34]. In $[\mathrm{Cd}(\mathbf{L}^2)_2](\mathrm{ClO_4})_2$ (**2**) each $\mathbf{L}^2$ binds via its four sulfur atoms to yield a sandwich-like arrangement in the form of an unusual S_8 distorted square antiprismatic coordination geometry [Fig. 2(b)].

In a different investigation, thermodynamic (potentiometric titration, polarographic and calorimetric) studies of the interaction of $\mathbf{L}^1$ with zinc(II), cadmium(II), mercury(II) and silver(I) were in accord with all three S-donors of this ligand interacting with each metal ion in acetonitrile when forming 1:1 (metal:ligand) complexes [35]. However, for silver(I), the data suggest that in the corresponding 1:2 complexes the respective $\mathbf{L}^1$ ligands are not both tridentate. The stability constants for this ligand system follow the order $\mathrm{Hg^{2+}} \gg \mathrm{Ag^{+}} > \mathrm{Cd^{2+}} \sim \mathrm{Zn^{2+}}$, with the enthalpy values following the same trend. Complementary DFT modelling of the respective metal ion-$\mathbf{L}^1$ systems was also reported.

Reflecting the tendency for palladium(II) (with its d^8 configuration) to form a square-planar complex in the presence of neutral ligand(s) and a coordinating anion such as a halogen, $\mathbf{L}^1$ yields a square-planar complex of type *cis*-$[\mathrm{Pd}(\mathbf{L}^1)\mathrm{Cl_2}]$ (**3a**). The X-ray structure of **3a** shows that only two of the three thioether donors of $\mathbf{L}^1$ are coordinated (Fig. 3) [36]. However, the remaining S atom is positioned above the $\mathrm{PdS_2Cl_2}$ coordination plane with an axial Pd-S long-range contact distance of 3.16 Å. The palladium(II) centre is also 3.53 Å from one S donor in an adjacent complex molecule.

A variable pressure X-ray structure study of **3a** showed that, on increasing the pressure to 4.4 GPa, a sudden transformation of the mononuclear square planar structure in **3a** to a zig-zag chain polymer (**3b**) (Fig. 4) occurred together with a marked conformational change in part of the backbone of the bound macrocycle. The in-plane Pd···S and above-plane Pd···S distances contract to 2.85 and 3.12 Å, respectively, to give each palladium(II) centre a pseudo-octahedral geometry. On lowering the pressure, the transformation is reversed.

Grant et al. published the X-ray structure of $[\mathrm{Pt}(\mathbf{L}^1)(\mathrm{tmphen})]\mathrm{PF_6}$ (**4**) (where tmphen is tetramethyl-1,10-phenanthroline) [37]; the