Multinuclear Structures

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Molecular Wheels of Ruthenium and Osmium with Bridging Chalcogenolate Ligands: Edge-Shared-Octahedron Structures and Metal-Ion Binding**

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Metal molecular wheels, herein referring to cyclic structures consisting of edge- or vertex-shared coordination polyhedra or polygons such as the octahedra shared in modes **a**–**d** and tetrahedra or squares shared in modes **f** and **g** in Figure 1, are among the fascinating types of self-assembled supramolecular architectures.[1] Notable examples include large single-strand wheels of polyoxometalates (up to M_{16}) based on **a**,[1a] metal carboxylate and alkoxide complexes (up to M_{18}) based on **c**–**e**,[1a–f] and metal thiolate complexes (up to M_{14}) based on **f** and **g**.[1a,f,h] In our endeavor to develop a general strategy to construct octahedron-based wheels including those of second- and third-row transition metals, we were attracted to the report by Hoffmann and Alemany[2] highlighting the key role of chalcogenolate bridging ligands in constructing metal molecular wheels. With the exception of $[\{Fe(TePh)_2(CO)_2\}_6]$,[3] the reported metal molecular wheels with bridging chalcogenolate ligands[1,4,5] are based on edge-shared squares (**g**) or tetrahedra (**f**).

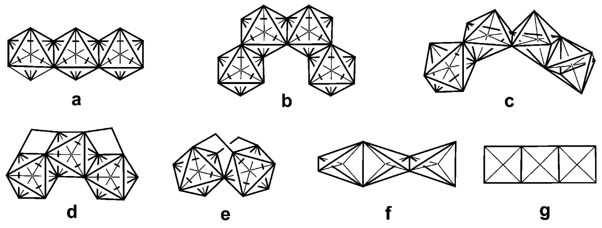

Figure 1. Examples of shared polyhedra or polygons in metal molecular wheels: *trans*-edge-shared (**a**, **f**, **g**), skew-edge-shared (planar M_n **b**, non-planar M_n **c**), and both vertex-linked and edge- (**d**) or vertex-shared (**e**).

Metal molecular wheels based on **b** can be traced back more than 70 years ago, to when Anderson postulated a structure for 6-heteropolyanions $[XMo_6O_{24}]^{n-}$ (Figure 2);[6] this proposed structure can be described as a **b**-based M_6 wheel binding a central X ion. Since then, many metal complexes with Anderson-type structure (**I**, Figure 2) have been known, particularly 6-heteropolyanions of molybdenum and tungsten,[7] along with some other complexes[8] such as iron μ-alkoxides[8a–d] and a uranium μ-phenylimido complex.[8e] Notably, occurrence of the Anderson-type structure devoid of the central X ion (i.e. M_6 wheel **II** in Figure 2) has also been well documented;[1f,g,3,9,10] an early example is the structure of β-$MoCl_4$ determined by Müller.[9] Saalfrank and co-workers obtained iron coronate $[CsFe_8L_8]^+$ (**III**, Figure 2),[8b] which contains a **b**-based M_8 wheel **IV** (Figure 2) that is supported by extensive ligand chelation and a large template (Cs^+).

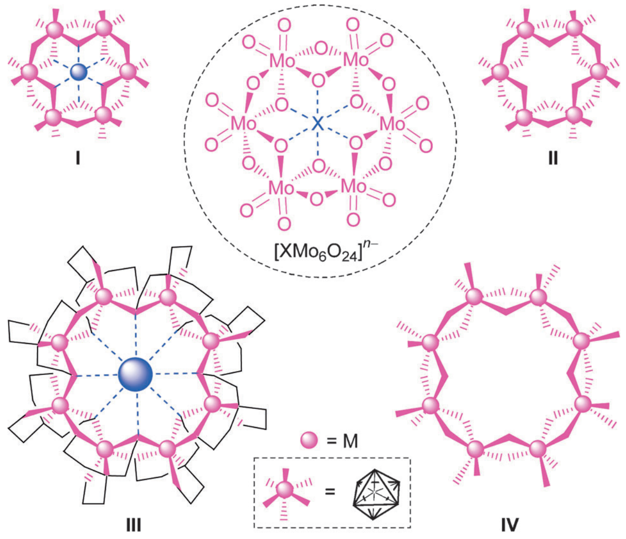

Figure 2. Anderson structure of $[XMo_6O_{24}]^{n-}$, Anderson-type structure **I**, M_6 wheel **II**, and their M_8 analogues **III** and **IV**.

An intriguing question arises: could an M_8 wheel **IV** that lacks the support of chelating ligands and template, be stable for isolation? Despite the isolation of self-assembled examples of **I** (containing a central metal ion) and **II**,[1,3,7–9] a stable, isolated M_6 wheel **II** that exhibits high affinity to bind metal

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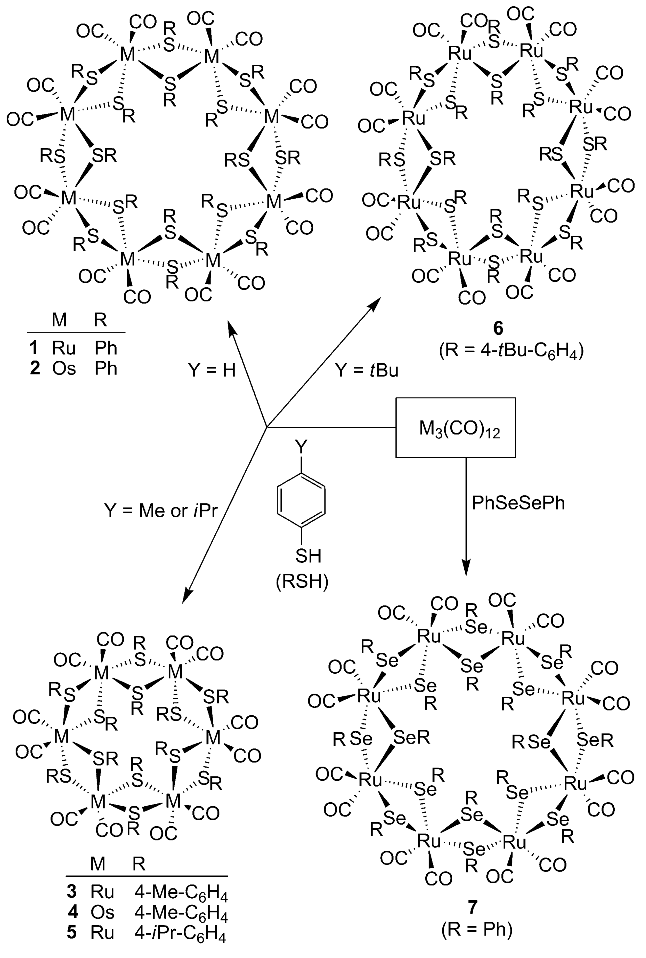
ion(s) is yet to be found. Herein we report a number of structurally characterized **b**-based ruthenium and osmium chalogenolate wheels, which to the best of our knowledge provide the first examples of an isolated M_8 wheel **IV**, and also a strong binding of coinage metal ion by an isolated M_6 wheel **II**.

Treatment of $M_3(CO)_{12}$ (M = Ru, Os) with PhSH under nitrogen at 120 or 150 °C for 12 h afforded $[\{M(SPh)_2(CO)_2\}_8]$ (M = Ru **1**, 85 % yield; M = Os **2**, 42 % yield; Scheme 1); $[\{M(SPh)_2(CO)_2\}_6]$ (M = Ru, Os) were not detected. But upon exchanging PhSH for 4-Y-C_6H_4SH (Y = Me, *i*Pr), similar reactions gave $[\{M\{S(4\text{-Me-}C_6H_4)\}_2(CO)_2\}_6]$ (M = Ru **3**, 65 % yield; M = Os **4**, 42 % yield) or $[\{Ru\{S(4\text{-}i\text{Pr-}C_6H_4)\}_2(CO)_2\}_6]$ (**5**, 41 % yield; Scheme 1) without the corresponding $[\{M(SR)_2(CO)_2\}_8]$. When 4-*t*Bu-C_6H_4SH was used, $[\{Ru\{S(4\text{-}t\text{Bu-}C_6H_4)\}_2(CO)_2\}_8]$ (**6**, 29 % yield) was obtained (Scheme 1). Reaction of $Ru_3(CO)_{12}$ with PhSeSePh at 150 °C for 12 h produced $[\{Ru(SePh)_2(CO)_2\}_8]$ (**7**, 60 % yield; Scheme 1) and $[\{Ru(SePh)_2(CO)_2\}_6]$ (**8**, 16 % yield). Detailed procedures for the isolation of **1**–**8** are described in the Supporting Information.



Scheme 1. Synthesis of **1**–**7**.

Complexes **1**–**8**, that is, $[\{M(ER)_2(CO)_2\}_n]$ ($n = 8$ or 6), have all been structurally characterized by X-ray crystal analysis[11] (see Figure 3 and Figures S1–S8 and Table S1 in the Supporting Information). These diamagnetic octahedral d^6 M^{II} complexes are stable in solution as well as in solid form; their ^{1}H NMR spectra in $CDCl_3$ did not significantly change with temperature (from −60 to 35 °C). The spectral features of **1**–**8** (see Figures S9–S21 in the Supporting Information) include 1) two sets of R signals of the μ-ER^- (E = S, Se) ligands in ^{1}H NMR spectrum and a prominent cluster peak attributed to $[M-CO]^+$ in the electrospray ionization (ESI) mass spectrum; 2) signals in the ^{13}C NMR spectrum at $\delta \approx 198$ and 180 ppm attributed to the coordinated CO ligands in the Ru and Os complexes, respectively; and 3) strong ν(CO) bands at 2021–2038 and 1952–1986 cm^{-1} in the IR spectra.

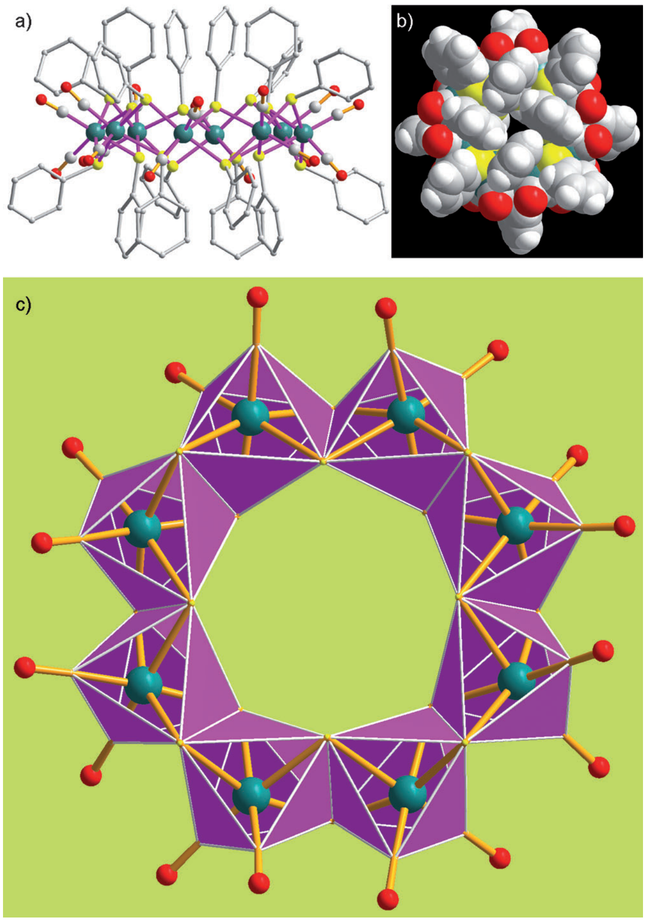


Figure 3. Structure of **2**. a) Side view (hydrogen atoms are not shown). b) Top view (space-filling representation). c) View of the Os_8S_{16} core comprising skew-edge-shared octahedra.

Octamers **1**, **2**, **6**, and **7** have the structure of M_8 wheel **IV**, whereas hexamers **3**–**5** and **8** have the structure of M_6 wheel **II**. These molecular wheels feature planar M_8 or M_6 arrangements constituting almost regular octagons or hexagons, respectively, except for **6**, which contains a significantly elongated Ru_8 octagon. The wheel size (defined as the average distance between two opposing M atoms in the M_n polygon) is 9.56–9.84 Å for the octamers, much larger than that of 7.40–7.68 Å for the hexamers. Large metal molecular wheels that contain planar M_n ($n = 8$ or even 10) polygons based on shared octahedra are not unprecedented, but the previously reported examples[1] are based on sharing modes **a**, **d**, **e** in Figure 1, except for the above-mentioned M_8 wheel moiety contained in **III**.[8b]

The preferential formation of M_8 wheels (**1** and **2**) and M_6 wheels (**3**–**5**) for RSH bearing *para* substituent H and Me (or *i*Pr), respectively, (Scheme 1) was unexpected. This wheel size modification is different from previously reported ones, such as the template method (by exchanging Li^+ or Na^+ for Cs^+) developed by Saalfrank and co-workers[8b] and the nontemplate method (by changing the μ-alkoxide ligand from MeO^- to $^-OCH_2CH_2CH_2O^-$) developed by Christou and co-workers.[12] Notably, to increase the wheel size of $[XFe_6(OMe)_{12}(L)_6]^+$ ($X = Li^+$, Na^+; L is a bidentate chelating ligand) belonging to structure **I**, Gatteschi and co-workers employed larger templates (K^+ or Cs^+) and obtained $[Fe_{12}(OMe)_{24}(L)_{12}]$[13] in approximately 20 % yield; this M_{12} wheel is nonplanar and is based on sharing mode **c** in Figure 1.

Density functional theory (DFT) calculations on model complexes $[\{Ru(SMe)_2(CO)_2\}_n]$ ($n = 6$, 8, 10; for optimized structures, see Figure S22 in the Supporting Information) revealed their relative energies (ΔE) to be −59.6, −58.8, −56.1 kcal mol^{-1} for $n = 6$, 8, 10, respectively. A similar trend was found for Gibbs free energies (Table S2 in the Supporting Information). Given the similar ΔE values for the Ru_6 and Ru_8 wheels and not much lower ΔE for Ru_{10}, the observed formation of $[\{M(SR)_2(CO)_2\}_8]$ (**1**, **2**, **6**) is not unreasonable, and we envision that an octahedron-based decanuclear molecular wheel $[\{Ru(SR)_2(CO)_2\}_{10}]$, may be attainable by tuning the R group. The frontier molecular orbitals of $[\{Ru(SMe)_2(CO)_2\}_n]$ ($n = 6$, 8, 10) are fairly similar (Figure 4). The highest occupied molecular orbitals (HOMOs) show a degree of characteristic localization on the central moiety of ring; high electron density is observed on p orbitals of the inner sulfur atoms. In contrast, the lowest unoccupied molecular orbitals (LUMOs) have delocalized σ* antibonding characteristics, which are derived from Ru d_{z^2} and p orbitals of the outer sulfur atoms of the whole molecular framework.

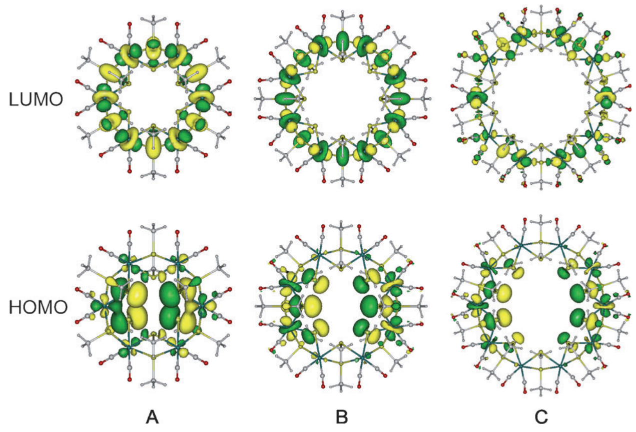


Figure 4. Kohn–Sham molecular orbital isodensity plots (isodensity value 0.03 a.u.) for model complexes $[\{Ru(SMe)_2(CO)_2\}_n]$ ($n = 6$ **A**, 8 **B**, 10 **C**).

$[\{M(SR)_2(CO)_2\}_n]$ can selectively bind coinage metal ions M'^+. Using isolated $[\{Ru(SR)_2(CO)_2\}_n]$ ($n = 6$, 8) as examples, no binding toward Li^+, Na^+, K^+, or Ca^{2+} was revealed by ESI-MS analysis. Interestingly, treatment of **5**, a typical example of $[\{M(SR)_2(CO)_2\}_6]$, with excess $AgCF_3SO_3$ or $[Cu^I(CH_3CN)_4]PF_6$ in chloroform for 30 min afforded $[M'\{Ru(S(4\text{-}i\text{Pr-}C_6H_4))_2(CO)_2\}_6]^+$ ($M' = Cu^+$ **5**-Cu, Ag^+ **5**-Ag; Figure 5), as revealed by ESI-MS and ^{1}H NMR and IR spectroscopy and confirmed by X-ray crystal structure determination[11] (Figure 5; Figures S23–S29 in the Supporting Information). For **6**, an example of $[\{M(SR)_2(CO)_2\}_8]$, ESI-MS analysis of its reaction mixture with $AgCF_3SO_3$ revealed a prominent cluster peak assignable to $[Ag\{Ru(S(4\text{-}t\text{Bu-}C_6H_4))_2(CO)_2\}_6]^+$ (Figure S30 in the Supporting Information), suggesting that **6** was unstable in the presence of Ag^+. The structure of **5**-Cu contains a planar three-coordinate Cu^I center, with shorter Cu–S distances (2.2086(11) Å) than in $[Cu^I(SPh)_3]^{2-}$ (2.274(4)–2.335(4) Å),[14] indicating a strong binding of Cu^+ by **5**. The Ru_6 wheel in **5**-Cu has geometrical parameters similar to those in **5** (see Table S3 in the Supporting Information). UV/Vis spectroscopy measurements revealed a red shift of the absorption bands of **5** upon treatment with $AgCF_3SO_3$ (see Figure S31 in the Supporting Information). The binding constants of **5** toward Cu^+ and Ag^+ were determined to be 1.7×10^4 and 2.0×10^4 M^{-1}, respectively, by the spectrophotometric method (see the Supporting Information).

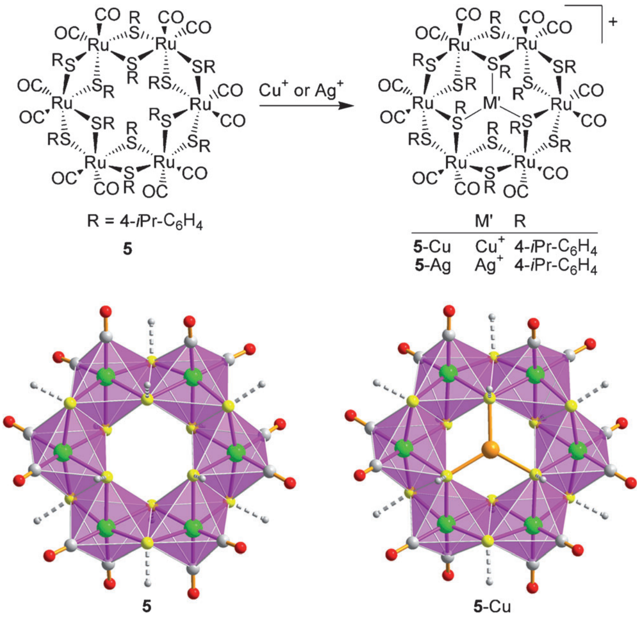


Figure 5. Top: Selective binding of coinage metal ions by **5**. Bottom: Structures of **5** and **5**-Cu (with omission of hydrogen atoms and aryl groups) showing the shared octahedra.

The in vitro biological activity of the molecular wheels has been explored using **5**. This complex exhibited $IC_{50} > 100$ μM to various kinds of human cells by Mosmann-based cytotoxic MTT assay[15] and could accumulate on the cell membrane after 4 h incubation at 100 and 200 μM by tube-formation assay using murine endothelial (MS1) cells (Figures S32 and S33 in the Supporting Information). Some **5** could be taken up by the MS1 cells, in which 0.16, 0.21, 3.46, and 0.02 ppb ruthenium per microgram protein were detected for 50, 100, 200 μм, and vehicle control, respectively, by inductively coupled plasma mass spectrometry. When **5** was used for carrying the coinage metal ion such as Ag^+, MTT assay using colorectal adenocarcinoma (SW480) cells revealed higher cytotoxicity of **5**-Ag than of **5** (43 % vs. < 10 % cancer cell death at 100 μм).

In summary, we have demonstrated the use of ruthenium and osmium chalcogenolate systems for self-assembly of interesting metal molecular wheels such as the **b**-based M_8 wheel **IV**. The isolation of M_6 or M_8 wheels **1–8** based on edge-shared octahedra, combined with reported metal thiolate wheels based on edge-shared tetrahedra or squares, highlights metal chalcogenolate coordination as an appealing strategy to construct metal molecular wheels. In view of the affinity of the M_6 wheel **5** to bind Cu^+ and Ag^+ ions ($K = (1.7–2.0) \times 10^4\,\text{M}^{-1}$), this type of molecular wheel would have useful application in selective metal ion binding through rational design.

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