

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

with bridging chalcogenolate ligands^[1,4,5] are based on edge-shared squares (**g**) or tetrahedra (**f**).

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]

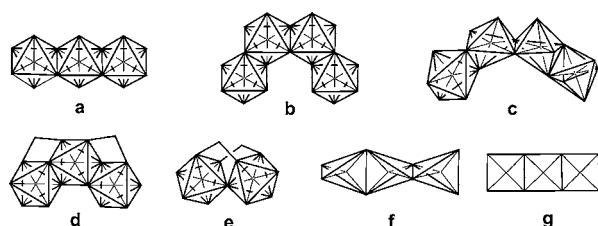


Figure 1. Examples of shared polyhedra or polygons in metal molecular wheels: *trans*-edge-shared (**a**, **f**, **g**), skew-edge-shared (planar M_n **b**, non-planar M_n **c**), and both vertex-linked and edge- (**d**) or vertex-shared (**e**).

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

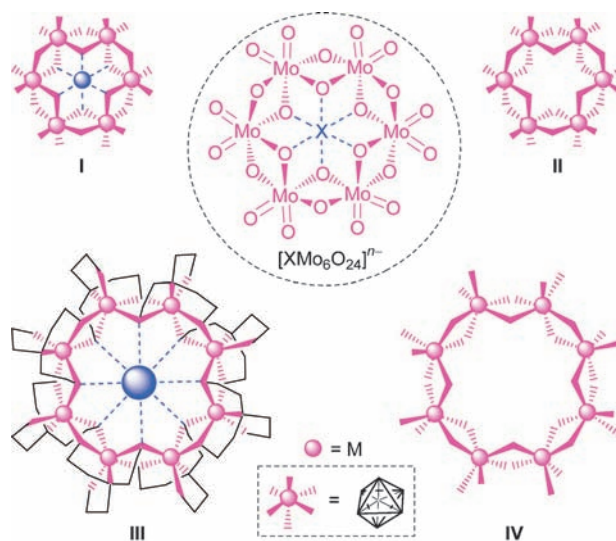


Figure 2. Anderson structure of $[XMo_6O_{24}]^{n-}$, Anderson-type structure I, M_6 wheel II, and their M_8 analogues III and IV.

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^+).

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

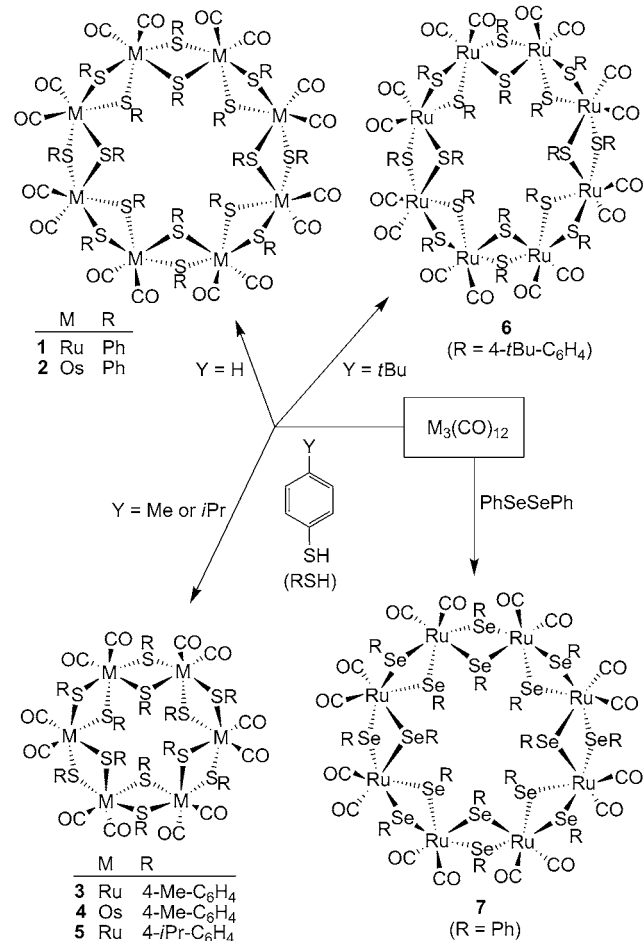
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ion(s) is yet to be found. Herein we report a number of structurally characterized **b**-based ruthenium and osmium chalenolate wheels, which to the best of our knowledge provide the first examples of an isolated M_8 wheel **IV**, and also a strong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

Treatment of $M_3(CO)_2$ ($M = Ru, Os$) with PhSH under nitrogen at 120 or 150 °C for 12 h afforded $[M(SPh)_2(CO)_2]_n$ ($M = Ru$ **1**, 85 % yield; $M = Os$ **2**, 42 % yield; Scheme 1);



Scheme 1. Synthesis of **1–7**.

$[M(SPh)_2(CO)_2]_n$ ($M = Ru, Os$) were not detected. But upon exchanging PhSH for 4- Y -C₆H₄SH ($Y = Me, iPr$), similar reactions gave $[M\{S(4-Me-C_6H_4)\}_2(CO)_2]_n$ ($M = Ru$ **3**, 65 % yield; $M = Os$ **4**, 42 % yield) or $[Ru\{S(4-*i*Pr-C_6H_4)\}_2(CO)_2]_n$ (**5**, 41 % yield; Scheme 1) without the corresponding $[M(SR)_2(CO)_2]_n$. When 4-*t*Bu-C₆H₄SH was used, $[Ru\{S(4-*t*Bu-C_6H_4)\}_2(CO)_2]_n$ (**6**, 29 % yield) was obtained (Scheme 1). Reaction of $Ru_3(CO)_2$ with PhSeSePh at 150 °C for 12 h produced $[Ru(SPh)_2(CO)_2]_n$ (**7**, 60 % yield; Scheme 1) and $[Ru(SPh)_2(CO)_2]_n$ (**8**, 16 % yield). Detailed procedures for the isolation of **1–8** are described in the Supporting Information.

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

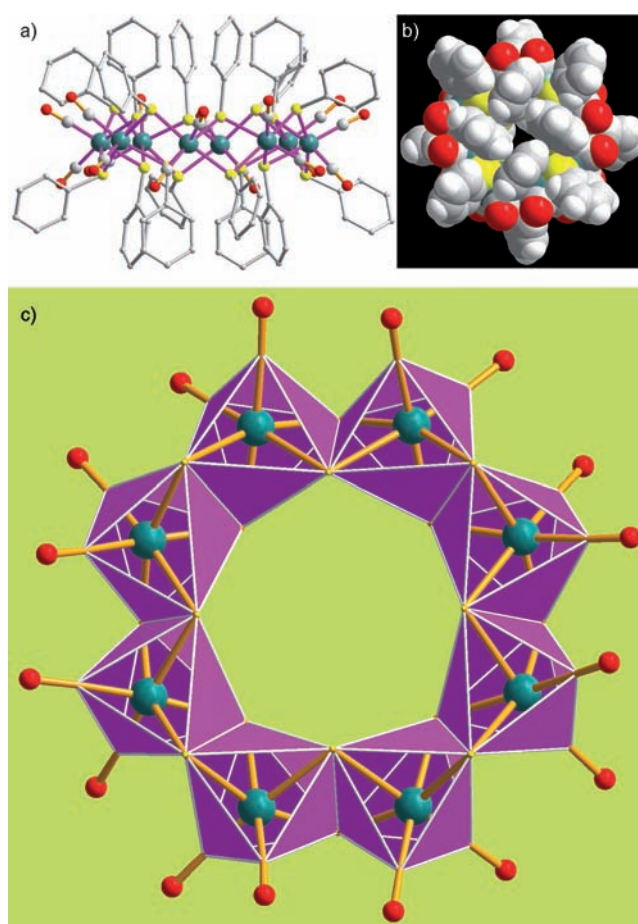


Figure 3. Structure of **2**. a) Side view (hydrogen atoms are not shown). b) Top view (space-filling representation). c) View of the Os_8S_{16} core comprising skew-edge-shared octahedra.

the Supporting Information). These diamagnetic octahedral $d^6 M^{II}$ complexes are stable in solution as well as in solid form; their 1H 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 1H 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 $\nu(CO)$ bands at 2021–2038 and 1952–1986 cm^{-1} in the IR spectra.

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 $[M(SR)_2(CO)_2]_n$ (**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

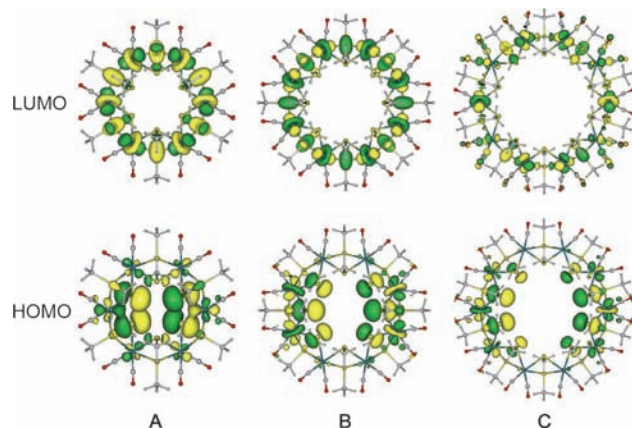


Figure 4. Kohn–Sham molecular orbital isodensity plots (isodensity value 0.03 a.u.) for model complexes $[Ru(SMe)_2(CO)_2]_n$ ($n=6$ **A**, **8** **B**, **10** **C**).

(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.

$[M(SR)_2(CO)_2]_n$ 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 $[M'\{Ru(S(4-*i*Pr-C_6H_4))_2(CO)_2\}_6]^+$ ($M'=Cu^+$ **5-Cu**, Ag^+ **5-Ag**; Figure 5), as revealed by ESI-MS and 1H NMR and IR

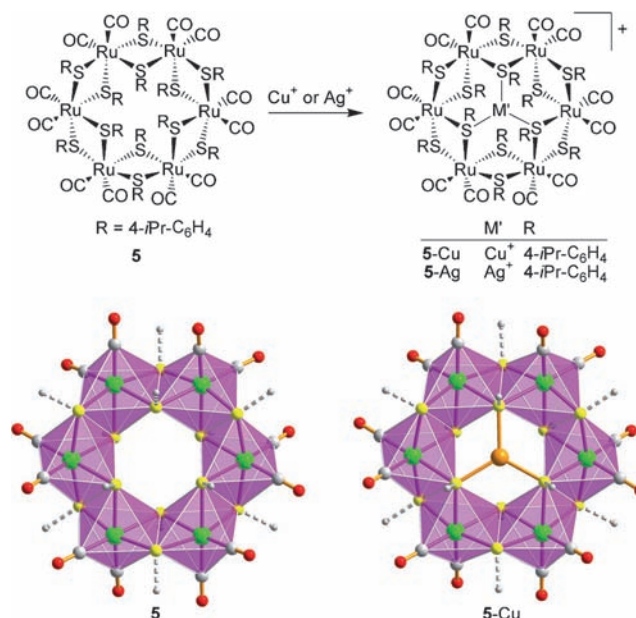


Figure 5. Top: Selective binding of coinage metal ions by **5**. Bottom: Structures of **5** and **5-Cu** (with omission of hydrogen atoms and aryl groups) showing the shared octahedra.

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 $[Ag\{Ru(S(4-*t*Bu-C_6H_4))_2(CO)_2\}_6]^+$ (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).

The *in vitro* biological activity of the molecular wheels has been explored using **5**. This complex exhibited $IC_{50} > 100$ μ M 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 μ M 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 μM , 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 μM).

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 ($K = (1.7\text{--}2.0) \times 10^4 \text{ M}^{-1}$), this type of molecular wheel would have useful application in selective metal ion binding through rational design.

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