J. Am. Chem. Soc. **2001,** *123,* 735−736

Spontaneous Formation of a Diamond-Crown Structure of Re_8 Polyselenide and a Cage Structure of Re_3 Polytelluride

Guo-Xin Jin,[†] Yasuhiro Arikawa, and Kazuyuki Tatsumi*

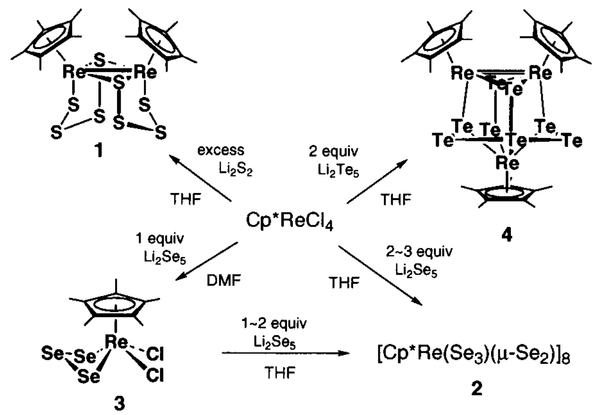
Research Center for Materials Science and
Department of Chemistry, Graduate School of Science
Nagoya University, Furo-cho
Chikusa-ku, Nagoya 464-8602, Japan

Received August 14, 2000

Chemistry of soluble transition metal chalcogenides represents one of the most fruitful specialties of coordination chemistry.[1] Owing to the ability of calcogenide dianions (E^{2-}) and polychalcogenide dianions (E_x^{2-}) to coordinate in various ways, a diverse range of soluble transition metal aggregates may be stabilized. Remarkable examples of such class are the high-nuclear binary metal sulfides, $[M_6S_{17}]^{4-}$ (M = Nb, Ta),[2] $[Cu_6(S_4)_3S_5]^{2-}$,[3] and $[Fe_{18}S_{30}]^{10-}$.[4] We have developed chemistry of organometallic trithio and triseleno complexes of Nb(V), Ta(V), Mo(V), and W(V), with a pentamethylcyclopentadienyl (Cp*) auxiliary.[5] As an outgrowth of our study on the group 5 and 6 metal complexes, we became interested in chalcogenido complexes of half-sandwich rhenium. A good number of mononuclear and dinuclear CpRe derivatives with chalcogenide and polychalcogenide ligands have been reported previously, for example, $Cp^*Re(O)(E_4)$ (E = S, Se), $Cp^*Re(S_3)(S_4)$, $Cp^*_2Re_2(\mu\text{-}E_4)_2$,[6] $[Cp'_2Re_2(\mu\text{-}S_2)_2]Cl_2$ ($Cp' = C_5EtMe_4$),[7] and $Cp^*Re(E_3)Cl_2$.[8]

From the reaction of Cp^*ReCl_4 with excess Li_2S_2 in THF, we were able to isolate only the known dinuclear complex $Cp^*_2Re_2(\mu\text{-}S_4)_2$ (**1**) as black crystals in 23% yield.[9] This complex was previously synthesized via desulfurization of $Cp^*Re(S_3)(S_4)$ with PPh_3.[6] Next we examined the reaction of Cp^*ReCl_4 with Li_2Se_5 which was prepared from elemental selenium and $LiBHEt_3$ in THF. A THF solution (20 mL) of Li_2Se_5 (0.75 mmol) and Cp^*ReCl_4 (0.185 g, 0.40 mmol) in the same solvent were combined and stirred for 24 h at room temperature. The resulting black solution was filtrated and dried in vacuo, and the residue was extracted by toluene (10 mL) and recrystallized from benzene/hexane to afford 0.21 g (73% yield) of product **2** as air/moisture-sensitive black prisms.[10] When the analogous reaction between Cp^*ReCl_4 and 1 equiv of Li_2Se_5 was carried out in DMF, the violet chloro/triselenido complex $Cp^*Re(Se_3)Cl_2$ (**3**) was generated.[8] This complex **3** was found to be converted into **2** in 56% isolated yield, upon treatment with 1−2 equiv of Li_2Se_5 in THF.

Scheme 1



An X-ray crystallographic study of the black crystals of **2** established the stoichiometry $Cp^*_8Re_8Se_{40}\cdot 4(C_6H_6)$,[11] and Figure 1 gives two views of the cluster. Compound **2** is a unique cyclic octanuclear cluster of diamond-crown shape and is the lateral dimensions of the cluster are ~13.9 (Se8− −Se16) × 12.7 (Se3− −Se11) Å. Each Re carries one Cp* ligand and one Se_3^{2-} chelate, and eight such $Cp^*Re(Se_3)$ units are linked by Se_2^{2-} groups. The cluster structure of **2** may be viewed as an ellipsoidal $[Re(\mu\text{-}Se_2)]_8$ 24-membered macrocycle, to which eight diamond-shaped $ReSe_3$ blades are placed inside the macrocycle and Cp* ligands coordinate at Re atoms from the outside. The oxidation state of every Re is V and its four-legged piano-stool coordination geometry makes it a 16-electron system. Every bridging Se_2^{2-} unit is bound to metal centers with a transoid configuration, where the Re−Se−Se−Re tortional angles range from 101.9(1)° to 125.6(1)°. Consequently, the Re atoms are alternatively situated upper and lower portions of the 24-membered macrocycle, as viewed from the side. It is interesting to note that the Se−Re−Se angles within the 24-membered ring (72.10(8)°−75.8(1)°) are notably smaller than the Se−Re−Se angles of the $ReSe_3$ blades (78.45(8)°−80.9(1)°), and that the Re−Se bond distances in the macrocycle (av 2.525 Å) are longer than those of the $ReSe_3$ blades (av 2.434 Å), while the Se−Se distances are not very different (24-membered ring, av 2.368 Å; blades, av 2.352 Å). The final Fourier map shows no strong residual peaks in the interior of the $[Re(\mu\text{-}Se_2)]_8$ macrocycle. The absence of Li cations in the macrocyclic structure of **2** contrasts to $[Fe_{18}S_{30}]^{10-}$ where two Na cations are encapsulated within the toroidal cavity, and

---

* Corresponding author. E-mail: i45100a@nucc.cc.nagoya-u.ac.jp.

[†] On leave from Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China.

(1) (a) Draganjac, M.; Rauchfuss, T. B. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 742−757. (b) Roof, L. C.; Kolis, J. W. *Chem. Rev.* **1993**, *93*, 1037−1080. (c) Ansari, M. A.; Ibers, J. A. *Coord. Chem. Rev.* **1990**, *100*, 223−266. (d) Herberhold, M.; Jin, G.-X.; Müller, A.; Penk, M. *Z. Naturforsch. B.* **1991**, *46*, 25−32. (e) Wachter, J. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1613−1626. (f) Tatsumi, K.; Kawaguchi, H.; Inoue, K.; Tani, K.; Cramer, R. E. *Inorg. Chem.* **1993**, *32*, 4317−4323.

(2) Sola, J.; Do, Y.; Berg, J. M.; Holm, R. H. *J. Am. Chem. Soc.* **1983**, *105*, 7784−7786.

(3) (a) Henkel, G.; Betz, P.: Krebs, B. *J. Chem. Soc., Chem. Commun.* **1984**, 314−315. (b) Müller, A.; Römer, M.; Bögge, H.; Krickemeyer, E.; Bergmann, D. *J. Chem. Soc., Chem. Commun.* **1984**, 348−349.

(4) You, J.-F.; Snyder, B. S.; Holm, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 6589−6591.

(5) (a) Tatsumi, K.; Inoue, Y.; Nakamura, A.; Cramer, R. E.; VanDoorne, W.; Gilje, J. W. *J. Am. Chem. Soc.* **1989**, *111*, 782−783. (b) Tatsumi, K.; Inoue, Y.; Kawaguchi, H.; Kohsaka, M.; Nakamura, A.; Cramer, R. E.; VanDoorne, W.; Taogoshi, G. J.; Richmann, P. N. *Organometallics* **1993**, *12*, 352−364. (c) Tatsumi, K.; Kawaguchi, H.; Tani, K. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 591−593. (d) Kawaguchi, H.; Yamada, K.; Lang, J.-P.; Tatsumi, K. *J. Am. Chem. Soc.* **1997**, *119*, 10346−10358. (e) Kawaguchi, H.; Tatsumi, K. *J. Chem. Soc., Chem. Commun.* **2000**, 1299−1300.

(6) (a) Herberhold, M.; Jin, G.-X.; Milius, W. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 85−87. (b) Herberhold, M.; Jin, G.-X.; Milius, W. *J. Organomet. Chem.* **1993**, *459*, 257−263.

(7) Rakowski DuBois, M.; Jagirdar, B. R.; Dietz, S.; Noll, B. C. *Organometallics* **1997**, *16*, 294−296.

(8) Herberhold, M.; Jin, G.-X.; Milius, W. *Z. Anorg. Allg. Chem.* **1994**, *620*, 299−303.

(9) (a) All reactions and manipulations were performed under Ar, using dry solvents. (b) Complex **1** was characterized by X-ray crystallography.[6a]

(10) For $[Cp^*Re(Se_3)(\mu\text{-}Se_2)]_8$ (**2**): ^1H NMR ($CDCl_3$) δ 1.96 (s, C_5Me_5); ^{13}C NMR ($CDCl_3$) δ 12.60 (s, C_5Me_5), 98.75 (s, C_5Me_5); IR (KBr pellet) 2956, 2898, 1371 cm^{-1}. Anal. Calcd for $C_{80}H_{120}Re_8Se_{40}$: C, 16.77; H, 2.11. Found: C, 16.01; H, 2.13.

(11) Diffraction data were collected on a Rigaku Mercury CCD system equipped with an ultraX-18 X-ray generator and an MSC d*TREK software package. An empirical absorption correction was made with the 4th3D+4th2D method of d*TREK. Crystal data for (**2**)·4(C_6H_6): monoclinic, $P2_1/c$ (No. 14), a = 18.1206(6) Å, b = 33.9535(3) Å, c = 24.0449(4) Å, β = 99.833(1)°, V = 14576.5(6) $Å^3$, Z = 4, D_c = 2.753 g/cm^3. From 33 450 total unique reflections, the structure was solved with 18 996 observed data ($2\theta_{max}$= 55.0°, with $I > 3.00\sigma(I)$) and 797 variables: R = 0.086, Rw = 0.091. A disorder was observed in the 24-membered macrocycle. Six Re atoms are disordered over two positions in the occupancy ratio of 80/20, each set of which is separated by 0.40−0.53 Å, and only the major arrangement is shown in Figure 1.

10.1021/ja003007p CCC: $20.00

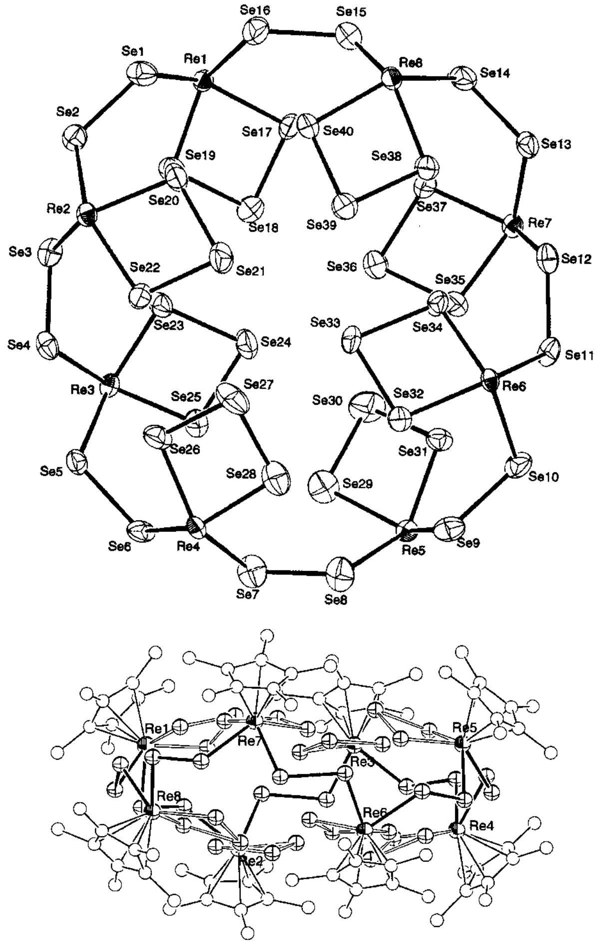


Figure 1. Two views of $[Cp^*Re(Se_3)(\mu\text{-}Se_2)]_8$ (**2**). Upper: planar projection, where Cp* groups are omitted for clarity. Lower: side view showing thickness of the molecule.

suggests that the unusual diamond-crown structure of **2** is formed spontaneously without a "template" effect of Li cations. Another feature of note is that the cluster is quite soluble in benzene and toluene despite the high nuclearity. We sense that eight Cp* ligands at the periphery of the $[Re(\mu\text{-}Se_2)]_8$ macrocycle promote the solubility. This property is also pertinent to the high solubility of a tricubane cluster $[Cp^*_2Mo_2Fe_2S_4]_3(\mu\text{-}S_4)_3$ in toluene.[12]

The reaction of Cp^*ReCl_4 with 2 equiv of Li_2Te_5 was also carried out. A deep red THF solution of Li_2Te_5, generated from Te (5.0 mmol) and $LiBHEt_3$ (2.0 mmol), was treated with Cp^*ReCl_4 for 3 h at room temperature. After a workup similar to the one used for the isolation of **2**, hexane (30 mL) was slowly layered onto a benzene solution (20 mL) of the crude product, and it was kept standing at −20 °C. Over a 3-week period, air/moisture-sensitive black prismatic crystals were grown to afford **4** in 27% yield.[13]

The crystals were subjected to X-ray analysis, and the molecular structure is shown in Figure 2.[14] Compound **4** is an unusual trinuclear cage cluster, consisting of two different types of Cp*Re units. Two Re atoms, Re2 and Re3 with a short metal−metal distance of 2.6641(8) Å, are doubly bridged by Te7 and Te8 and are further coordinated by Te6 and Te2, respectively. On the other hand, Re1 is bound to four Te atoms. The ^1H NMR spectrum in $CDCl_3$ consists of two singlets of Cp* protons in 1:2 ratio, indicating that the structure of **4** in crystals is retained in solution. The five Te atoms (Te2−Te3−Te4−Te5−Te6) are approximately planar, and the maximum deviation from the least-squared plane occurs at Te4 (0.234 Å). The Te−Te distances are grouped into three categories: Te1−Te7, Te2−Te3, Te5−Te6 (2.778(2)−2.812(2) Å); Te4−Te8, Te3−Te4, Te4−Te5 (2.971(2)−2.995(2) Å); Te1−Te2, Te1−Te6 (3.326(2), 3.325(2) Å). The distances of the first category are comparable to the known Te−Te single-bond lengths in various polytellurides coordinated to metal centers,[1c] while those of the third category are somewhat too long to invoke strong bonding interactions. The Te−Te distances of the second category are enigmatic, like those found in the intriguing structures of Cs_2Te_5,[15] $Te_6(AsF_6)_4$,[16] and $(PPh_4)_3[NbTe_{10}]$.[17] Since the Re1−Te4 distance of 2.732 Å is at the longest end of the Re−Te bonds in **4**, Te4 cannot be regarded as a terminal Te^{2-} ligand, and there must be partial bonding interactions between Te4 and the three neighboring Te atoms.

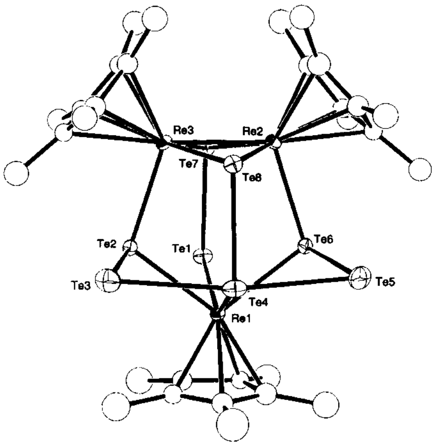


Figure 2. Structure of $Cp^*_3Re_3Te_8$ (**4**). Selected bond distances (Å): Re1−Te1 2.763(1), Re1−Te2 2.682(1), Re1−Te4 2.732(1), Re1−Te6 2.684(1), Re2−Te6 2.719(1), Re2−Te7 2.577(1), Re2−Te8 2.605(1), Re3−Te2 2.720(1), Re3−Te7 2.578(1), Re3−Te8 2.605(1).

Oxidation state of III is electronically feasible for Re2 and Re3, in **4**, and they are relevant to the 18-electron Re(III) centers of $Cp^*_2Re_2(\mu\text{-}E_4)_2$ with a Re−Re double bond. If we make an extreme assumption that the Te−Te pairs of the second category, viz., Te4−Te8, Te3−Te4, and Te4−Te5, are nonbonding, it would create two Te^{2-} ligands and three Te_2^{2-} ligands, which gives rise to Re1(VII), Re2(III), and Re3(III). The Re1(VII) center is an electron-deficient 14-electron system, and four electrons have to be provided from the telluride ligands, to make it 18-electron. This can be done by formation of three 2/3-bonds between the Te−Te pairs of the second category, and the oxidation state of Re1 would become III. We think that the actual oxidation states of Re are between Re1(VII)−Re2(III)−Re3(III) with the $2Te^{2-} + 3Te_2^{2-}$ ligand set and Re1(III)−Re2(III)−Re3(III) with the $Te_6^{4-} + Te_2^{2-}$ ligand set.

Acknowledgment. We thank Professor Roger E. Cramer for careful inspection of the X-ray analysis.

Supporting Information Available: X-ray crystallographic files (CIF) for $(\mathbf{2})\cdot 4(C_6H_6)$ and $(\mathbf{4})\cdot C_6H_6$ (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA003007P

---

[12] Kawaguchi, H.; Yamada, K.; Ohnishi, S.; Tatsumi, K *J. Am. Chem. Soc.* **1997**, *119*, 10871−10872.

[13] For $Cp^*_3Re_3Te_8$ (**4**): ^1H NMR ($CDCl_3$) δ 2.15 (s, 30H, C_5Me_5), 1.94 (s, 15H, C_5Me_5); IR (KBr pellet) 2975, 2890, 1374 cm^{-1}. Anal. Calcd for $C_{30}H_{45}Re_3Te_8$: C, 18.15; H, 2.28. Found: C, 17.66; H, 2.42.

[14] Diffraction data were collected on a Rigaku RASA-7 Quantum system equipped with an ADSC CCD detector and an MSC d*TREK software package. An empirical absorption correction was made with the 4th3D+4th2D method of d*TREK. Crystal data for $(\mathbf{4})\cdot C_6H_6$: monoclinic, $P2_1$ (No. 4), a = 12.407(3) Å, b = 15.238(4) Å, c = 12.403(1) Å, β=107.085(1)°, V = 2241.2(6) $Å^3$, Z = 2, D_c = 3.057 g/cm^3. From 5226 total unique reflections, the structure was solved with 4721 observed data ($2\theta_{max}$= 55.0°, with $I > 3.00\sigma(I)$) and 244 variables: R = 0.034, Rw = 0.043.

[15] Böttcher, P.; Kretschmann, U. *Z. Anorg. Allg. Chem.* **1982**, *491*, 39−46.

[16] Burns, R. C.; Gillespie, R. J.; Luk, W.-C.; Slim, D. R. *Inorg. Chem.* **1979**, *18*, 3086−3094.

[17] Flomer, W. A.; Kolis, J. W. *J. Am. Chem. Soc.* **1988**, *110*, 3682−3683.