Octahedral Arrangement of Porphyrin Moieties around Hexarhenium(III) Cluster Cores: Structure of (μ_3-Selenido)hexa-(5-(4-pyridyl)-10,15,20-tritolylporphyrin)-hexarhenium(III) (2+)**

Ai Itasaka[+], Masaaki Abe, Takashi Yoshimura, Kiyoshi Tsuge, Masamitsu Suzuki, Taira Imamura,* and Yoichi Sasaki*

In memoriam Ai Itasaka

Hexanuclear rhenum(III) cluster complexes are the subject of extensive current studies[1–17] because of their redox and photoluminescent properties as well as the versatility of the design of the coordination environment around the hexarhenium cores, $Re_6(\mu_3\text{-}E)_8$ (E = S, Se). The cores may be regarded as a giant octahedral center, since the six terminal ligands are oriented in such a manner that each pair of neighboring ligands are arranged vertically to each other. It is possible to mimic the chemistry of simple octahedral metal complexes by using the hexarhenium cluster core, as ligand substitution at the six terminal sites of the core can be controlled with respect to the number and geometrical arrangements of the terminal ligands. Examples are the preparation of a series of pyridine (py) complexes, $[Re_6(\mu_3\text{-}S)_8Cl_n(py)_{6-n}]^{(2-n)+}$ ($n = 2-4$), which included the isolation of two isomers (*cis* and *trans*) for $n = 2$,[4, 13] and the bridge-chelate formation around the core by a long-chain bidentate ligand, $(C_6H_5)_2P(CH_2)_6P(C_6H_5)_2$.[14] Another important aspect of using a giant octahedral center is to arrange as many as six sterically bulky ligands around the core, something that is difficult around a single metal center. In the past few years, we have been studying the preparation and properties of some oligomeric porphyrins that are constructed through coordination of pyridylporphyrins to metalloporphyrins.[18–26] Although the octahedral arrangement of the porphyrin ligands is interesting as an important structural motif and also as a building block of certain supramolecular complexes, it is too bulky to make stable six-coordinate mononuclear metal complexes. We now show that the octahedral arrangement of porphyrins is possible by using the hexarhenium cores. The new complexes **1**–**4** (H_2PyT_3P = 5-(4-pyridyl)-10,15,20-tritolylporphyrin) are reported herein.

$[Re_6(\mu_3\text{-}S)_8(H_2PyT_3P)_6]^{2+}$ **1**

$[Re_6(\mu_3\text{-}S)_8(ZnPyT_3P)_6]^{2+}$ **2**

$[Re_6(\mu_3\text{-}Se)_8(H_2PyT_3P)_6]^{2+}$ **3**

$[Re_6(\mu_3\text{-}Se)_8(ZnPyT_3P)_6]^{2+}$ **4**

The complexes **1** and **3** containing free-base porphyrins were prepared by the substitution of 5-(4-pyridyl)-10,15,20-tritolylporphyrin for the solvent molecules in $[Re_6(\mu_3\text{-}S)_8(CH_3CN)_6]^{2+}$ and $[Re_6(\mu_3\text{-}Se)_8(CH_3CN)_6]^{2+}$, respectively, in chlorobenzene. Zinc(II) ions were introduced into the porphyrins in **1** and **3** by reacting them with zinc acetate in CH_2Cl_2 to give **2** and **4**, respectively.

The structure of **3**-$(SbF_6)_2$ was determined by single-crystal X-ray structure analysis.[27] Figure 1 shows the remarkable structure of **3**. Six H_2PyT_3P groups coordinate to the $[Re_6Se_8]^{2+}$ core through the pyridyl group. The bond lengths and angles in the $[Re_6Se_8]^{2+}$ core reveal that the rhenium selenide cluster core has virtually O_h symmetry as in other hexarhenium chalcogenide complexes.[3, 7–14, 28–34] The complex ion has a cystallographically imposed inversion center. In addition, six H_2PyT_3P groups are arranged essentially in a C_3 manner around the $[Re_6Se_8]^{2+}$ core (Figure 1). Therefore, the complex ion in the crystal has virtual S_6 symmetry. Because the H_2PyT_3P group itself has C_{2h} symmetry in the highest symmetrical form and can rotate freely around the Re–N bond without mutual steric interactions, the most symmetric structure of the complex ion should be D_{3d}, D_{2h}, or D_{2d}. The S_6 structure is derived from the D_{3d} structure by a slight rotation of the porphyrin ligands. Thus, the ideal D_{3d} structure seems to be distorted by the effect of crystal packing. The cation **3** represents the remarkable class of compounds with six porphyrins in one molecule, the structure of which has been resolved by X-ray structure analysis.

^1H NMR spectra in $CDCl_3$ of the complexes show that all six porphyrin ligands in each complex are equivalent at room temperature. Temperature dependence of the ^1H NMR spectra of **1** is complicated by proton exchange within the porphyrin rings and a possible kinetic rotational barrier of the Re–N bond.

Visible absorption spectra of the new complexes in CH_2Cl_2 are dominated by strong absorption bands of the porphyrin ligands. All the complexes display a strong Soret band at 422–423 nm with $\varepsilon = 2.5 \times 10^5\,mol^{-1}\,dm^{-3}$ per ligand, which may be compared with the corresponding band of the free porphyrin at 418 nm ($\varepsilon = 5.0 \times 10^5\,mol^{-1}\,dm^{-3}$). The band in the complexes is somewhat broader than that of the free ligand, which suggests appreciable electronic interactions among the ligands. The four Q bands in the region 500–700 nm were observed for the complexes **1** and **3**, the number of Q bands reduced to two on introduction of Zn^{II} centers into the porphyrin ring (**2** and **4**).

Cyclic voltammograms of the complexes in CH_2Cl_2 show the redox waves of the porphyrin moieties in the range -2.0–

---

[*] Prof. Dr. Y. Sasaki, Prof. Dr. T. Imamura, A. Itasaka[+], Dr. M. Abe, Dr. T. Yoshimura,[++] Dr. K. Tsuge, M. Suzuki
Division of Chemistry
Graduate School of Science
Hokkaido University
Kita-ku, Sapporo, 060-0810 (Japan)
Fax: (+81) 11-706-3447
E-mail: ysasaki@sci.hokudai.ac.jp, timamura@sci.hokudai.ac.jp

[+] Deceased October 6, 2001.

[++] Present address:
Department of Chemistry, Faculty of Engineering
Gunma University
Tenjin-cho 1-5-1, Kiryu, Gunma 376-8515 (Japan)

[**] This work was supported by a Grant-in-Aids for Scientific Research No. 10149102 (Priority Area of "Metal-Assembled Complexes") from the Ministry of Education, Science, Sports, and Culture of Japan. Helpful suggestions from Dr. Tetsuaki Fujihara of this laboratory are gratefully acknowledged. The authors are also grateful to Prof. Dr. Noboru Kitamura, Dr. Shoji Ishizaka, and Mr. Kazunori Ogawa of this Department for the photophysical measurements.

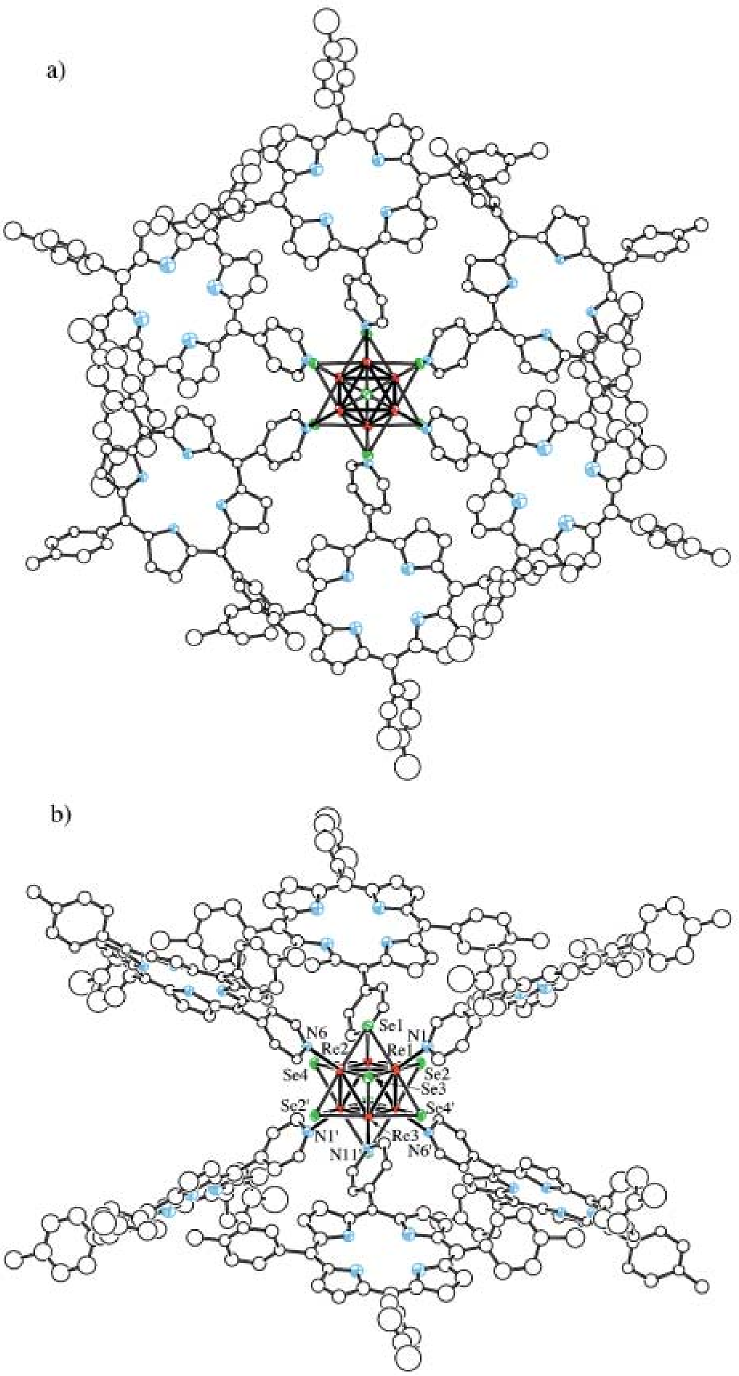
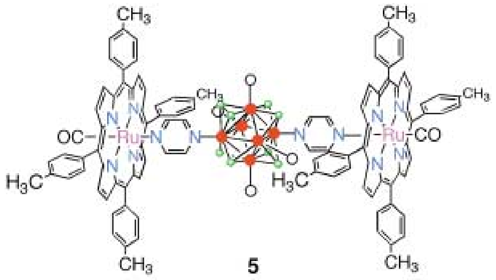


Figure 1. Structure of **3** in **3**-$(SbF_6)_2 \cdot CH_2Cl_2 \cdot 1.6\,C_5H_{12}$ (ORTEP drawing; thermal elipsoids at the 30% probability level). a) Top view, b) side view. Red: rhenium, blue: nitrogen, green: selenium. The crystallographically imposed inversion center is at the center of the Re_6 octahedron. Selected interatomic distances [Å] and bond angles [°] around the central core: Re-Re: 2.571(2)–2.606(2) (av 2.582); Re-Se: 2.486(4)–2.501(3) (av. 2.483); Re-N: 2.14(2)–2.20(3) (av 2.16); Re-Re-Re$_{(60)}$: 59.42(6)–60.76(5) (av 60.00); Re-Re-Re$_{(90)}$: 89.48(7)–90.52(7) (av. 90.00); Re-Se-Re: 62.1(1)–63.4(1) (av 62.7); Se-Re-Se$_{(90)}$: 89.3(1)–90.6(1) (av 90.0); Se-Re-Se$_{(180)}$: 176.4(1)–177.1(2) (av 176.7); Se-Re-N: 90.3(7)–93.1(7) (av 91.7).

+1.7 V versus Ag/AgCl. The redox potentials of the Re_6^{III}/$Re_5^{III}Re^{IV}$ process for the $Re_6(\mu_3\text{-}S)_8$ and $Re_6(\mu_3\text{-}Se)_8$ complexes shift towards positive potentials on increasing the number of pyridyl ligands in place of the terminal halides. The cyclic voltammogram of the $Re_6(\mu_3\text{-}Se)_8$ complex **3** exhibits a shoulder at the positive side of the porphyrin second oxidation wave at +1.33 V (versus Ag/AgCl), which may be ascribed to the core oxidation.[4, 13] The voltammogram of the free ligand displays two reversible reduction waves and one reversible and one irreversible oxidation wave in CH_2Cl_2. Upon coordination of the porphyrin ligand to the hexarhenium core, these waves show only a small shift. The second oxidation wave becomes reversible. There is no sign of the splitting in each wave, which suggests no significant redox interaction among the porphyrin ligands both for the oxidation and the reduction processes. It has been found previously that the hexarhenium core can mediate redox interactions of coordinated ligands as exemplified by the splitting of the reduction waves of the ligands L (4-cyanopyridine, pyrazine, 4,4′-bipyridine, etc.) coordinated to the apices of the hexarhenium(III) core.[13] It may be that the perpendicular orientation of the pyridyl group and the porphyrin ring in **1**–**4** prevents effective redox communication among the porphyrin-ring parts of the six ligands.

We have also prepared new complexes, **5**,[35] **6**, and **7** (where H_2ttp = 5,10,15,20-tetra(tolyl)porphyrin; pz = pyrazine; bpy = 4,4′-bipyridine; Scheme 1) in which the redox waves of the two ttp ligands do not show any sign of splitting, while those of the bridging pyrazine or 4,4′-bipyridine show small splitting ($\Delta E = 0.14$ V).[13] Here also perpendicular orientation of the bridging pyrazine ligand and the porphyrin ring in **5**–**7** would be relevant.



Scheme 1. Schematic structure of **5**.

trans-$[Re_6(\mu_3\text{-}S)_8Cl_4\{(\mu\text{-pz})Ru(CO)(ttp)\}_2]^{2-}$ **5**

trans-$[Re_6(\mu_3\text{-}S)_8Cl_4\{(\mu\text{-bpy})Ru(CO)(ttp)\}_2]^{2-}$ **6**

cis-$[Re_6(\mu_3\text{-}S)_8Cl_4\{(\mu\text{-bpy})Ru(CO)(ttp)\}_2]^{2-}$ **7**

Hexarhenium(III) complexes are known to be photoluminescent.[3, 5, 6, 13, 14, 16, 36–40] The new porphyrin complexes **1**–**4** are also emissive, but the short lifetimes for **3**-$(BF_4)_2$ in CH_2Cl_2 and the shape of double-maximum emission spectrum suggested that the emission originates from the porphyrin moieties.

The successful arrangement of porphyrin ligands in the octahedral arrangement around the hexarhenium(III) core makes further design of the supramolecular architecture possible. The work to introduce porphyrins with more than two pyridyl moieties around the hexarhenium(III) core, as well as to bring various metal ions into the porphyrins in the present complexes, is underway.

Experimental Section

UV/Vis absorption spectra were recorded on a Hitachi U3410 and U3000 spectrophotometer. Cyclic voltammetry was performed with a BAS-50W potentiostat and a software package. The working and counter electrodes were a glassy-carbon disk and a platinum wire, respectively. Cyclic voltammograms were recorded at a scan rate of 100 mV s^{-1}. The reference electrode was Ag/AgCl against which the half-wave potential of ferrocene/ferrocunium ion (Fc/Fc$^+$; $E_{1/2}$(Fc$^{+/0}$)) was 0.43 V. ^{1}H NMR spectra were recorded at 22 °C on a JEOL JNM-EX270 NMR spectrometer.

1-$(BF_4)_2$: [$Re_6S_8(CH_3CN)_6$]$(BF_4)_2$[41] (100 mg ; 5.58×10^{-5} mol) and H_2PyT_3P (218 mg, 3.35×10^{-4} mol) were heated under reflux in chlorobenzene (10 mL) for two days (the former was suspended in the solution), and then solvent was removed under reduced pressure. The resulting solid was dissolved in CH_2Cl_2, and the solution was purified by chromatography on a silica gel column. After the elution of H_2PyT_3P with 0.4 % CH_3OH/CH_2Cl_2, the complex cation **1** was eluted with 3 % CH_3OH/CH_2Cl_2. The eluate was evaporated to dryness and the residue was dried in vacuo. Yield: 80 mg (26 %); elemental analysis calcd (%) for $C_{276}H_{210}N_{30}B_2F_8S_8Re_6$: C 60.34, H 3.85, N 7.65; found: C 60.52, H 4.12, N 7.42; ^{1}H NMR (270 MHz, $CDCl_3$, TMS): $\delta = -2.73$ (s, 12 H; NH); 2.68 (s, 36 H; CH_3), 2.70 (s, 18 H; CH_3); 8.85 (s, 24 H; H_β), 9.00 (d, 12 H; H_β), 9.12 (d, 12 H; H_β); 8.09 (d, 36 H; *o*-H); 7.54 (d, 36 H; *m*-H); 10.47 (d, 12 H; 2,6-H of py); 8.69 (d, 12 H; 3,5-H of py).

2-$(BF_4)_2$: [$Re_6S_8(H_2PyT_3P)_6$]$(BF_4)_2$ (**1**-$(BF_4)_2$; 40 mg; 7.33×10^{-6} mol) was dissolved in CH_2Cl_2 (10 mL) and was added to $Zn(CH_3COO)_2 \cdot 2H_2O$ (9.7 mg; 4.40×10^{-5} mol) dissolved in minimum amount of CH_3OH. The solution was heated under reflux for 1 h, and was evaporated under reduced pressure. The resulting solid was dissolved in CH_2Cl_2, and filtered through Celite. The complex was obtained by diffusing pentane to the solution. Yield: 36 mg (84 %); elemental analysis calcd (%) for $C_{276}H_{198}N_{30}B_2F_8S_8Zn_6Re_6$: C 56.43, H 3.40, N 7.15; found: C 56.39, H 3.61, N 7.09. ^{1}H NMR (270 MHz, $CDCl_3$, TMS): $\delta = 2.68$ (s, 36 H; CH_3), 2.70 (s, 18 H; CH_3); 8.96 (s, 24 H; H_β), 9.09 (d, 12 H; H_β), 9.19 (d, 12 H; H_β); 8.09 (d, 36 H; *o*-H); 7.52 (d, 24 H; *m*-H), 7.55 (d, 12 H; *m*-H); 10.45 (d, 12 H; 2,6-H of py); 8.69 (d, 12 H; 3,5-H of py).

3-$(BF_4)_2$: [$Re_6Se_8(CH_3CN)_6$]$(BF_4)_2$[31] (100 mg; 4.61×10^{-5} mol) and H_2PyT_3P (180 mg, 2.77×10^{-4} mol) were heated under reflux in chlorobenzene (5 mL) for 20 h (the former was suspended in the solution), and then the solvent was removed under reduced pressure. The resulting solid was dissolved in CH_2Cl_2, and the solution was purified by chromatography on a silica gel column. After the elution of unreacted H_2PyT_3P with 0.4 % CH_3OH/CH_2Cl_2, **3** was eluted with 3 % CH_3OH/CH_2Cl_2. The eluate was evaporated and the residue was recrystallized from CH_2Cl_2/diethyl ether. The purple product was collected by filtration and washed with pentane and then dried in vacuo. Yield: 35 mg (12 %); elemental analysis calcd (%) for $C_{276}H_{210}N_{30}B_2F_8Se_8Re_6$: C 56.48, H 3.61, N 7.16; found: C 56.59, H 3.87, N 7.03; ^{1}H NMR (270 MHz, $CDCl_3$, TMS): $\delta = -2.74$ (s, 12 H; NH); 2.68 (s, 36 H; CH_3), 2.70 (s, 18 H; CH_3); 8.86 (s, 24 H; H_β), 9.00 (d, 12 H; H_β), 9.13 (d, 12 H; H_β); 8.09 (d, 36 H; *o*-H); 7.54(d, 36 H; *m*-H); 10.72(d, 12 H; 2,6-H of py); 8.55(d, 12 H; 3,5-H of py).

3-$(SbF_6)_2$: This was prepared by using [$Re_6Se_8(CH_3CN)_6$]$(SbF_6)_2$ in place of [$Re_6Se_8(CH_3CN)_6$]$(BF_4)_2$.[42]

4-$(BF_4)_2$: [$Re_6Se_8(H_2PyT_3P)_6$]$(BF_4)_2$ (**3**-$(BF_4)_2$; 100 mg; 1.70×10^{-5} mol) was dissolved in CH_2Cl_2 (15 mL) and was added to $Zn(CH_3COO)_2 \cdot 2H_2O$ (22 mg; 1.02×10^{-4} mol) dissolved in minimum amount of CH_3OH. The solution was heated under reflux for 30 min, and was evaporated under reduced pressure. The resulting solid was dissolved in CH_2Cl_2, and filtered through Celite. The solid complex was obtained by diffusing pentane into the solution. Yield: 99 mg (93 %); elemental analysis calcd (%) for $C_{276}H_{198}N_{30}B_2F_8Se_8Zn_6Re_6$: C 53.04, H 3.19, N 6.72; found: C 52.76, H 3.35, N 6.59. ^{1}H NMR (270 MHz, $CDCl_3$, TMS): $\delta = 2.67$ (s, 36 H; CH_3), 2.71 (s, 18 H; CH_3); 8.96 (s, 24 H; H_β), 9.09 (d, 12 H; H_β), 9.21 (d, 12 H; H_β); 8.09 (d, 36 H; *o*-H); 7.53 (d, 24 H; *m*-H), 7.55(d, 12 H; *m*-H); 10.71 (d, 12 H; 2,6-H of py); 8.57 (d, 12 H; 3,5-H of py). ESI-MS: *m*/*z*: 53038 [$M - 2(BF_4)$]$^{2+}$.

$(Bu_4N)_2$-**5**, $(Bu_4N)_2$-**6**, and $(Bu_4N)_2$-**7**: The pyrazine (pz) complex, $(Bu_4N)_2${*trans*-[$Re_6S_8Cl_4(pz)_2$]} (20 mg, 0.0093 mmol),[13] and [Ru(ttp)(CO)(CH_3OH)] (15.4 mg, 0.00186 mmol) were dissolved in CH_2Cl_2 (10 mL). The solution was stirred for 1 h at room temperature, toluene (4 mL) was then added, and was left for several days at room temperature to allow for evaporation. Purple crystals were obtained which were collected by filtration and washed with a mixture of CH_3CN and diethyl ether, and dried in vacuo. Yield of $(Bu_4N)_2$-**5:** 24 mg (69 %). The μ-4,4′-bipyridine analogues $(Bu_4N)_2$-**6** and $(Bu_4N)_2$-**7** were obtained similarly by using $(Bu_4N)_2${*trans*-[$Re_6S_8Cl_4$(4,4′-bipyridine)$_2$]} and $(Bu_4N)_2${*cis*-[$Re_6S_8Cl_4$(4,4′-bipyridine)$_2$]}, respectively, in place of $(Bu_4N)_2${*trans*-[$Re_6S_8Cl_4(pz)_2$]}.

Received: September 17, 2001 [Z17912]

---

[1] J.-C. P. Gabriel, K. Boubekeur, S. Uriel, P. Batail, *Chem. Rev.* **2001**, *101*, 2037–2066.

[2] R. Wang, Z. Zheng, *J. Am. Chem. Soc.* **1999**, *121*, 3549–3550.

[3] T. Yoshimura, S. Ishizaka, K. Umakoshi, Y. Sasaki, H.-B. Kim, N. Kitamura, *Chem. Lett.* **1999**, 697–698.

[4] T. Yoshimura, K. Umakoshi, Y. Sasaki, A. G. Sykes, *Inorg. Chem.* **1999**, *38*, 5557–5564.

[5] T. Yoshimura, S. Ishizaka, Y. Sasaki, H.-B. Kim, N. Kitamura, N. G. Naumov, M. N. Sokolov, V. E. Fedorov, *Chem. Lett.* **1999**, 1121–1122.

[6] T. G. Gray, C. M. Rudzinski, D. G. Nocera, R. H. Holm, *Inorg. Chem.* **1999**, *38*, 5932–5933.

[7] Z. Zheng, T. G. Gray, R. H. Holm, *Inorg. Chem.* **1999**, *38*, 4888–4895.

[8] M. P. Shores, L. G. Beauvais, J. R. Long, *J. Am. Chem. Soc.* **1999**, *121*, 775–779.

[9] M. P. Shores, L. G. Beauvais, J. R. Long, *Inorg. Chem.* **1999**, *38*, 1648–1649.

[10] L. G. Beauvais, M. P. Shores, J. R. Long, *J. Am. Chem. Soc.* **2000**, *122*, 2763–2772.

[11] Y. V. Mironov, V. E. Fedorov, C. C. McLauchran, J. A. Ibers, *Inorg. Chem.* **2000**, *39*, 1809–1811.

[12] Y. V. Mironov, A. V. Virovets, N. G. Naumov, V. N. Ikorskii, V. E. Fedorov, *Chem. Eur. J.* **2000**, *6*, 1361–1365.

[13] T. Yoshimura, K. Umakoshi, Y. Sasaki, S. Ishizaka, H.-B. Kim, N. Kitamura, *Inorg. Chem.* **2000**, *39*, 1765–1772.

[14] Z.-N. Chen, T. Yoshimura, M. Abe, Y. Sasaki, S. Ishizaka, H.-B. Kim, N. Kitamura, *Angew. Chem.* **2001**, *113*, 245–248; *Angew. Chem. Int. Ed.* **2001**, *40*, 239–242.

[15] H. D. Selby, Z. Zheng, T. G. Gray, R. H. Holm, *Inorg. Chim. Acta* **2001**, *312*, 205–209.

[16] Z.-N. Chen, T. Yoshimura, M. Abe, K. Tsuge, Y. Sasaki, S. Ishizaka, H.-B. Kim, N. Kitamura, *Chem. Eur. J.* **2001**, *7*, 4447–4455.

[17] M. V. Bennet, L. G. Beauvais, M. P. Shores, J. R. Long, *J. Am. Chem. Soc.* **2001**, *123*, 8022–8032.

[18] A. Kimura, K. Funatsu, T. Imamura, H. Kido, Y. Sasaki, *Chem. Lett.* **1995**, 207–208.

[19] K. Funatsu, A. Kimura, T. Imamura, Y. Sasaki, *Chem. Lett.* **1995**, 765–766.

[20] K. Funatsu, A. Kimura, T. Imamura, A. Ichimura, Y. Sasaki, *Inorg. Chem.* **1997**, *36*, 1625–1635.

[21] K. Funatsu, T. Imamura, A. Ichimura, Y. Sasaki, *Inorg. Chem.* **1998**, *37*, 4986–4995.

[22] K. Funatsu, T. Imamura, A. Ichimura, Y. Sasaki, *Inorg. Chem.* **1998**, 1798–1804.

[23] N. Kariya, T. Imamura, Y. Sasaki, *Inorg. Chem.* **1997**, *36*, 833–839.

[24] N. Kariya, T. Imamura, Y. Sasaki, *Inorg. Chem.* **1998**, *37*, 1658–1660.

[25] T. Imamura, K. Funatsu, S. Ye, Y. Morioka, K. Uosaki, Y. Sasaki, *J. Am. Chem. Soc.* **2000**, *122*, 9032–9033.

[26] T. Imamura, K. Fukushima, *Coord. Chem. Rev.* **2000**, *198*, 133–156.

[27] Diffusion of pentane into CH_2Cl_2 solution of **3**-$(SbF_6)_2$ afforded thin fragile crystals, which were carefully mounted on a glass capillary and checked for singularity. Crystal data for **3**-$(SbF_6)_2 \cdot CH_2Cl_2 \cdot 1.6\,C_5H_{12}$ ($C_{285}H_{231.2}N_{30}Cl_2F_{12}Re_6Sb_2Se_8$): $M_r = 6367.67$, triclinic, space group $P\bar{1}$ (no. 2), $a = 16.510(2)$, $b = 24.023(5)$, $c = 24.639(6)$ Å, $\alpha = 114.596(9)$, $\beta = 103.752(3)$, $\gamma = 97.584(4)^\circ$, $V = 8330(2)$ Å^3, $Z = 1$; $\rho_{calcd} = 1.269$ g cm^{-3}; crystal dimensions $0.25 \times 0.13 \times 0.05$ mm^3; $\mu(Mo_{K\alpha}) =$

3.27 mm^{-1}; $T = 98$ K, $2\theta_{max} = 54°$. Data were collected on a Mercury CCD area detector coupled with a Rigaku AFC-8S diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation (0.7107 Å) using CrystalClear (Rigaku Co.). Total reflections collected 30371. Data were corrected for Lorentz and polarization effects. An empirical absorption correction was applied by using REQABA (min./max. transmission: 0.61/1.01). The structures were solved on a Silicon Graphics O2 computer system using teXsan, version 1.11 (Molecular Structure Co.). The initial position of rhenium atoms were determined by direct methods and other atoms were located using Fourier and difference Fourier techniques. Re, Sb, and Se atoms were refined anisotropically. Other non-hydrogen atoms were refined isotropically. With the exception of hydrogen atoms of crystal solvents, all hydrogen atoms were located at the calculated positions. One tolyl group was refined by using a rigid model. Full-matrix least-square refinement was employed against *F*. Final *R* and R_w values were 0.084 and 0.122 for 8842 observed reflections ($I > 3.5\sigma(I)$) and 735 variable parameters. Max./min. residual electron density were 2.87/−1.60 e Å^{-3}, both near Re atoms. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-170237. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[28] J. R. Long, A. S. Williamson, R. H. Holm, *Angew. Chem.* **1995**, *107*, 248–251; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 226–229.

[29] J. R. Long, L. S. McCarty, R. H. Holm, *J. Am. Chem. Soc.* **1996**, *118*, 4603–4616.

[30] Z. Zheng, R. H. Holm, *Inorg. Chem.* **1997**, *36*, 5173–5178.

[31] Z. Zheng, J. R. Long, R. H. Holm, *J. Am. Chem. Soc.* **1997**, *119*, 2163–2171.

[32] N. G. Naumov, A. V. Virovets, M. N. Sokolov, S. B. Artemkina, V. E. Fedorov, *Angew. Chem.* **1998**, *110*, 2043–2045; *Angew. Chem. Int. Ed.* **1998**, *37*, 1943–1945.

[33] M. W. Willer, J. R. Long, C. C. McLauchlan, R. H. Holm, *Inorg. Chem.* **1998**, *37*, 328–333.

[34] L. G. Beauvais, M. P. Shores, J. R. Long, *Chem. Mater.* **1998**, *10*, 3783–3786.

[35] A preliminary X-ray structural analysis of **5** revealed the suggested structure. (T. Yoshimura, unpublished result).

[36] R. Arratia-Perez, L. Hernandez-Acevedo, *J. Chem. Phys.* **1999**, *110*, 2529–2532.

[37] R. Arratia-Perez, L. Hernandez-Acevedo, *J. Chem. Phys.* **1999**, *111*, 168–172.

[38] C. Guilbaud, A. Deluzet, B. Domercq, P. Molinie, C. Coulon, K. Boubekeur, P. Batail, *Chem. Commun.* **1999**, 1867–1868.

[39] H. Honda, T. Noro, K. Tanaka, E. Miyoshi, *J. Chem. Phys.* **2001**, *114*, 10791–10797.

[40] L. Alvarez-Thon, L. Hermandez-Acevedo, R. Arratia-Perez, *J. Chem. Phys.* **2001**, *115*, 726–730.

[41] $[Re_6S_8(CH_3CN)_6](BF_4)_2$ was prepared from $(Bu_4N)_3[Re_6S_8I_6]$ in a manner similar to the μ_3-Se analogue.[31]

[42] $[Re_6S_8(CH_3CN)_6](SbF_6)_2$ was prepared by the method used to prepare $[Re_6Se_8(CH_3CN)_6](BF_4)_2$[31] but using $AgSbF_6$ in place of $AgBF_4$.

Photochemical Formation of Tire-Shaped Molybdenum Blues: Topology of a Defect Anion, $[Mo_{142}O_{432}H_{28}(H_2O)_{58}]^{12-}$**

Toshihiro Yamase* and Petra V. Prokop

UV irradiation (corresponding to the O→Mo ligand-to-metal charge-transfer photoexcitation) of isopolyoxomolybdates in aqueous solutions containing electron donors (such as alkylammonium cations, alcohols, and aliphatic carboxylates) results in formation of high-nuclearity mixed-valence species as a result of reduction self-assembly processes based on the dehydrative condensation at $[Mo^VO_5(OH)]$ sites produced photochemically in the polyoxomolybdate lattice:[1, 2] $[Mo_7O_{24}]^{6-}$ and β-$[Mo_8O_{26}]^{4-}$, which are dominant species at pH levels of 5.4 and 3.3 respectively, are converted into $[Mo_{14}O_{46}]^{10-}$ ($\{Mo_{14}\}$) $= [(Mo^VMo^{VI}_6O_{23})_2]^{10-}$ and $[H_{14}Mo_{37}O_{112}]^{12-} = \{[H_{10}Mo^V_{12}O_{40}(Mo^{VI}O_2)_3][H_2Mo^V_6Mo^{VI}_5O_{33}]_2\}^{12-}$, respectively.

In our extension of the solution photolysis of isopolyoxomolybdates to $[Mo_{36}O_{112}(H_2O)_{16}]^{8-}$ ($\{Mo_{36}\}$), which is the dominant species at pH 1–2 and higher-Mo concentrations ($\geq 10^{-2}$ M), we found the photochemical formation of a variety of car-tire-shaped giant molybdenum blues. These were also formed by thermal reduction[3–8] of Na_2MoO_4 with reducing agents such as iron, ascorbic acid, $NH_2OH \cdot HCl$, $N_2H_4 \cdot H_2SO_4$, and $Na_2S_2O_4$ under strongly acidic conditions (pH ≈ 1). The structure of $\{Mo_{36}\}$ consists of a centrosymmetric arrangement of two $\{Mo_{18}\}$ subunits, each of which is viewed as a Mo_7O_{24} group encircled by edge- and corner-shared MoO_6 octahedra (Figure 1).[9] We describe here a diamagnetic blue 28-electron reduced species ($\{Mo_{142}\}$ **1a**) produced photochemically through the degradative self-assembly of $\{Mo_{36}\}$ and discuss size and shape for the ring clusters derived from $\{Mo_{36}\}$ on the basis of the successive two-electron reduction dehydrative–condensation processes similar to the reductive dimerization of $[Mo_7O_{24}]^{6-}$ to $\{Mo_{14}\}$.[1]

$$[Mo^V_{28}Mo^{VI}_{114}O_{432}H_{28}(H_2O)_{58}]^{12-} \qquad \mathbf{1a}$$

The title anion (Figure 2a) has been isolated as $[NH_3iPr]^+$ salt **1**[10–12] the structure of which is quite similar to that reported for $Na_{26}[Mo^V_{28}Mo^{VI}_{114}O_{432}H_{14}(H_2O)_{58}] \cdot$ ca. $300\,H_2O$ thermally produced in the $Na_2MoO_4 \cdot 2H_2O/Na_2SO_4/N_2H_4 \cdot H_2SO_4/H_2SO_4$ system.[4]

$$[NH_3iPr]_{10}H_2[Mo^V_{28}Mo^{VI}_{114}O_{404}(OH)_{28}(H_2O)_{58}] \cdot 90\,H_2O \qquad \mathbf{1}$$

---

[*] Prof. Dr. T. Yamase, Dr. P. V. Prokop
Chemical Resources Laboratory
Tokyo Institute of Technology
4259 Nagatsuta, Midori-ku
Yokohama 226-8503 (Japan)
Fax: (+81) 45-924-5260
E-mail: tyamase@res.titech.ac.jp

[**] Photochemical studies of alkylammonium molybdates, Part 11. This work was supported by Grants-in-Aid for Scientific Research, No. 10304055 from the Ministry of Education, Science, Sports, and Culture and for Research project No. 99P01201 from RFTF/JSPS. We thank Dr. Kunihisa Sugimoto for help with intensity data measurements on a Rigaku/MSC Mercury CCD diffractometer at Rigaku Corporation. Part 10: Ref. [2].

1433-7851/02/4103-0466 $ 17.50+.50/0