η^3-Coordination of Hexadentate *N,N,N′,N′*-Tetrakis(2-pyridylmethyl)ethylenediamine (tpen) to a Mononuclear *fac*-$Re^{VII}O_3$ Center. The Isolation of a New Class of Metal-containing Ligands

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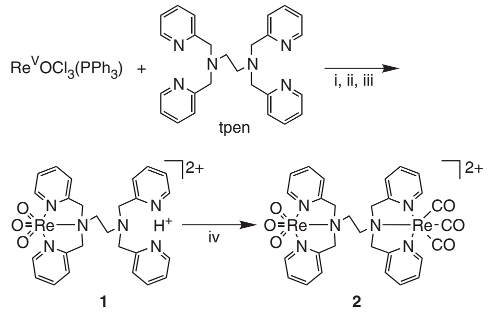
Reaction of $Re^VOCl_3(PPh_3)_2$ with an equimolar amount of tpen affords *fac*-$[Re^{VII}O_3(\eta^3\text{-tpenH})](ClO_4)_2$ (**1**), in which the tpen ligand coordinates to the *fac*-$Re^{VII}O_3$ center in a η^3-mode, and the dangling bis(2-pyridylmethyl)amine arm in **1** is subsequently used to produce a heterobimetallic complex *fac*-,*fac*-$[Re^{VII}O_3(\mu\text{-}\eta^3{:}\eta^3\text{-tpen})Re^I(CO)_3](ClO_4)_2$.

Transition metal complexes of multidentate ligands in which fewer than the maximum number of donor atoms are coordinated, thus containing coordination-free donor atom(s),[1] are potential metal-containing ligands to yield polynuclear compounds with a wide range of structures and functions. *N,N,N′,N′*-Tetrakis(2-pyridylmethyl)ethylenediamine,[2] abbreviated as tpen, is a hexadentate ligand which typically produces fully coordinated (η^6) mononuclear metal complexes[3] and homobimetallic complexes.[4] Interestingly, by varying metal ions and reaction conditions, η^5- and η^4- modes which afford one and two dangling pyridyl residues, respectively, are obtained.[5] Among the tpen–metal complex family, however, there is no example in which tpen coordinates to a single metal center in a η^3 tridentate mode. In such a compound, the other end of tpen is expected to bind an additional metal center to yield a range of tpen-bridged bimetallic complexes, which will be of considerable interest in the preparation of multifunctional molecular systems. From this viewpoint, the development of any simple approach to prepare mononuclear complexes containing η^3-tpen is essential.

Here we report a promising new approach to the η^3-coordination mode of tpen around a *fac*-$Re^{VII}O_3$ center. We show synthesis and successful characterization of *fac*-$[ReO_3(\eta^3\text{-tpenH})](ClO_4)_2$ (**1**) (tpenH is a protonated form of tpen, see below), in which the dangling bis(2-pyridylmethyl)amine (PY2) arm acts as a η^3 *tridentate* chelate to yield a tpen-bridged heterobimetallic complex.

A reaction sequence, together with the synthetic conditions, is illustrated in Scheme 1. Reaction of $Re^VOCl_3(PPh_3)_2$ (1.00 g, 1.12 mmol) with an equimolar amount of tpen (0.51 g, 1.12 mmol) in ethanol/water mixture (100 cm^3/4 cm^3) for 10 h in air at reflux temperature yielded a deep red solution, which contains seven-coordinated $[Re^{IV}O(\eta^6\text{-tpen})]^{2+}$ (including a fully coordinated tpen) as a major species.[6] After passing through the column, a 10-equivalent amount of $NaClO_4$ (1.18 g) was added to the main fraction for crystallization of products. Upon slow evaporation (10 days), colorless crystals of **1**[7] were obtained (yield, 39%). We suggest that a key to the success in the isolation of **1** is the intermediate formation of $[Re^{IV}O(\eta^6\text{-tpen})]^{2+}$ under the present synthetic conditions. Upon oxidation of Re^{IV} to Re^{VII} during the long-term crystallization process, the metal center leaves only three coordination sites for tpen, so that the unusual η^3-tpen coordination mode in **1** is obtained. Here, the excess amount of ClO_4^- or the air (as possible oxidants) and/or disproportionation reactions of $[Re^{IV}O(\eta^6\text{-tpen})]^{2+}$ are responsible for the formation of the Re^{VII} complex **1**.



Scheme 1. Synthetic scheme for **1** and **2**. Reagents and conditions: (i) ethanol/water (25/1, v/v), reflux, 10 h; (ii) column chromatography using SP-Sephadex resign and 1 M NaCl aq. as an eluent; (iii) 10 equiv. of $NaClO_4$; (iv) $Re^I(CO)_5Br$, CH_3CN, reflux, 2 h. All metal complexes are isolated as their ClO_4^- salts.

The crystals suitable for X-ray structural determination were grown from the aqueous solution by slow evaporation. The molecular structure of **1**, shown in Figure 1, clearly demonstrates that the "*fac*-ReO_3" center is chelated by one of two PY2 moieties of tpen in the η^3 tridentate fashion while the other end remains uncoordinated.[8] To the best of our knowledge, this

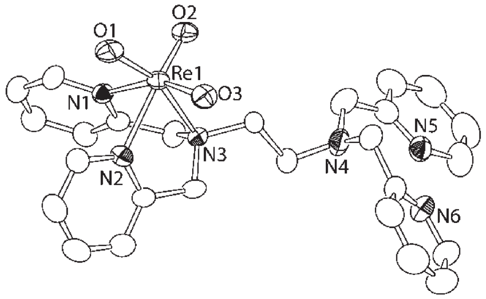


Figure 1. ORTEP drawing of the cationic portion in **1** at 50% probability level with the atomic numbering scheme. Hydrogen atoms are omitted for clarity. Selected interatomic lengths (Å) and bond angles (°): Re1–O1 1.738(4); Re1–O2 1.725(4); Re1–O3 1.722(4); Re1–N1 2.231(4); Re1–N2 2.229(4); Re1–N3 2.303(4); O1–Re1–O2 104.9(2); O1–Re1–O3 105.4(2); O2–Re1–O3 105.7(2); O1–Re1–N1 89.3(2); O1–Re1–N2 89.9(2); O1–Re1–N3 159.4(2); O2–Re1–N1 88.2(2); O2–Re1–N2 156.4(2); O2–Re1–N3 87.2(2); O3–Re1–N1 155.9(2); O3–Re1–N2 156.0(2); O3–Re1–N2 87.3(2); N1–Re1–N2 73.5(2); N1–Re1–N3 74.2(2); N2–Re1–N3 73.8(2).

is the first crystallographic characterization of a mononuclear metal complex containing tpen with the η^3 mode.[9] Re1 adopts a distorted octahedral geometry with the N_3O_3 donor set. Considering that the Re ion, the oxo ligand, and tpen have charges of $+7$, -2, and 0, respectively, the $+1$ charge per $\{ReO_3(\eta^3\text{-tpen})\}$ unit is provided. Given that there are two ClO_4^- anions per $\{ReO_3(\eta^3\text{-tpen})\}$ in the X-ray structure, which is further supported by satisfactory elemental analysis, it is reasonable to assume that the required $+2$ overall charge is fulfilled by the existence of one proton shared by nitrogen donors in the dangling PY2 moiety. Consistent with this picture, the three nitrogen atoms (N4, N5, and N6) sit in a close proximity each other (2.75–2.83 Å) owing to the hydrogen bonding interactions (this proton, however, was not observed in the final Fourier map). The Re–O distances [1.722(4)–1.738(4) Å], which fall into the typical range observed in the $fac\text{-}Re^{VII}O_3$ moiety,[10] along with the ν(Re=O) stretching frequency (924 cm^{-1}) rule out the possibility of protonation at one of the oxo groups.

The PY2 dangling moiety in **1** can be used as a tridentate chelate to yield homo- and heterobimetallic complexes. To verify this concept, we employed the reaction of **1** (101 mg, 0.12 mmol) with an equivalent amount of $[Re^I(CO)_5Br]$ (48 mg, 0.12 mmol) in refluxing CH_3CN (30 cm^3) for 2 h and obtained a heterobimetallic complex, $fac\text{-},fac\text{-}[Re^{VII}O_3(\mu\text{-}\eta^3{:}\eta^3\text{-tpen})Re^I(CO)_3](ClO_4)_2$ (**2**), as a colorless solid (yield, 79% based on **1**; Scheme 1).[11] Complex **2** is remarkable in that it contains two identical metal atoms, Re, with two extreme formal charges, $+7$ and $+1$. The infrared spectrum of **2** shows ν(CO) due to the $Re(CO)_3$ moiety at 2032 and 1930 cm^{-1} along with the ν(Re=O) due to the ReO_3 moiety at 924 cm^{-1}. FAB mass spectrometry reveals the molecular ion peak at $m/z = 1029$, which corresponds to the calculated value for $[ReO_3(\mu\text{-tpen})Re(CO)_3](ClO_4)^+$. Further, we observe signals at $m/z = 929$ and 695, which are assigned to $[ReO_3(\mu\text{-tpen})Re(CO)_3]^+$ and $[Re(CO)_3(tpen)]^+$, respectively. Together with π–π^* transitions due to tpen, complex **2** shows metal-to-ligand charge-transfer (MLCT) transitions associated with the $Re(CO)_3$ chromophore[12] at 302 nm (sh, $\varepsilon = 6900\ M^{-1}\ cm^{-1}$) in CH_3CN. We find through multiple synthetic experiments that the metal/ligand ratio employed here (e.g., Re^V/tpen = 1/1) plays an important role for the efficient formation of **1**. An attempt to prepare a homobimetallic complex from **1** and $n\text{-}Bu_4NReO_4$ was unsuccessful.

^1H NMR spectra of **1**[7] and **2**[11] show eight pyridyl resonances with an equivalent intensity ratio as well as four types of methylene resonances due to the tpen ligand, reflecting the asymmetric molecular structures. We note that for **1** and **2** there is no evidence for dissociation of pyridyl groups from the metal center(s)[13] or dynamic exchange between the coordinated and uncoordinated pyridyl groups in solution.[14]

By employing **1** as a metal-containing tridentate ligand, we believe that a diverse array of multinuclear species with intriguing chemical properties will be evolved. Thus, synthetic efforts to incorporate a range of transition-metal centers into **1** are now in progress.

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References and Notes

1 E. C. Constable, *Prog. Inorg. Chem.*, **42**, 67 (1994).

2 J. B. Mandel, C. Maricondi, and B. E. Douglas, *Inorg. Chem.*, **27**, 2990 (1988).

3 a) H.-R. Chang, J. K. McCusker, H. Toftlund, S. R. Wilson, A. X. Trautwein, H. Winkler, and D. N. Hendrickson, *J. Am. Chem. Soc.*, **112**, 6814 (1990). b) K. Kanamori, E. Kameda, and K. Okamoto, *Bull. Chem. Soc. Jpn.*, **69**, 2901 (1996). c) L. R. Morss and R. D. Rogers, *Inorg. Chim. Acta*, **255**, 193 (1997). d) H.-Y. Jin, M. Akiba, K. Umakoshi, Y. Sasaki, and K. Kabuto, *Acta Crystallogr., Sect. C*, **53**, 60 (1997).

4 a) A. Neves, K. Wieghardt, B. Nuber, and J. Weiss, *Inorg. Chim. Acta*, **150**, 183 (1988). b) S. Pal, J. W. Gohdes, W. C. A. Wilisch, and W. H. Armstrong, *Inorg. Chem.*, **31**, 713 (1992). c) R. Hazama, K. Umakoshi, A. Ichimura, S. Ikari, Y. Sasaki, and T. Ito, *Bull. Chem. Soc. Jpn.*, **68**, 456 (1995).

5 M. Sokolov, K. Umakoshi, and Y. Sasaki, *Inorg. Chem.*, **41**, 6237 (2002), and references cited therein.

6 This complex and the one-electron oxidized Re^V counterpart, $[Re^VO(\eta^6\text{-tpen})]^{3+}$, were fully characterised by spectroscopic methods along with X-ray crystallography. Details will be described elsewhere: H.-Y. Jin, S. Ikari, K. Kobayashi, K. Umakoshi, H. Sugimoto, Y. Sasaki, and T. Ito, in preparation.

7 **1**: Anal. Calcd for $C_{26}H_{29}Cl_2N_6O_9Re\cdot 2H_2O$: C, 34.94; H, 3.62; N, 9.40; Cl%, 7.93. Found: C, 34.86; H, 3.42; N, 9.55; Cl, 7.85%. ^1H NMR (270 MHz, CD_3CN) δ 8.84 (2H, d, ReO_3-py α-H; 2H, d, free py α-H), 8.17 (2H, t, free py γ-H), 8.06 (2H, t, ReO_3-py γ-H), 7.68 (2H, t, free py β-H; 2H, d, free py δ-H), 7.54 (2H, t, ReO_3-py β-H), 7.49 (2H, t, ReO_3-py δ-H), 4.84 (4H, q, ReO_3-pyCH_2N), 4.34 (4H, s, free pyCH_2N), 4.16 (2H, t, ReO_3-py$CH_2NCH_2CH_2N$), 3.49 (2H, t, free py$CH_2NCH_2CH_2$). UV-vis (CH_3CN) λ_{max}/nm (ε/$M^{-1}\ cm^{-1}$): 260 (15 900), 239 (sh, 13 500).

8 Crystal data of **1**: $M_r = 3599.16$, monoclinic; space group $P2_1/a$ (No. 14), $a = 14.636(2)$ Å, $b = 13.765(2)$ Å, $c = 17.999(3)$ Å, $\beta = 96.992(3)°$, $V = 3599(1)$ Å^3, $Z = 4$, $D_{calcd} = 1.74\ g\ cm^{-2}$; $\mu = 3.595\ mm^{-1}$; 19769 measured reflections, an empirical absorption correction was applied (min/max transmission factor = 0.350/1.000), 7530 unique reflections ($R_{int} = 0.03$), of which 6583 were observed ($I > 2\sigma(I)$); $R1 = 0.060$, $wR2 = 0.083$. X-ray diffraction data were collected on a Mercury CCD area detector with a Rigaku AFC-8S diffractometer using a graphite monochromated Mo Kα ($\lambda = 0.7107$ Å) at 295 K. Crystallographic data reported in this paper have been deposited to Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-201604.

9 Tpen which bridges identical metal centers in a $\mu\text{-}\eta^3{:}\eta^3$-mode (without other bridging ligands) is reported: a) R. R. Gagné, R. P. Kreh, J. A. Dodge, R. E. Marsh, and M. McCool, *Inorg. Chem.*, **21**, 254 (1982). b) S. Pal and W. H. Armstrong, *Inorg. Chem.*, **31**, 5417 (1992).

10 a) K. Wieghardt, C. Pomp, B. Nuber, and J. Weiss, *Inorg. Chem.*, **25**, 1659 (1986). b) W. A. Herrmann, P. W. Roesky, F. E. Kühn, M. Elison, G. Artus, W. Scherer, C. C. Romão, A. Lopes, and J.-M. Basset, *Inorg. Chem.*, **34**, 4701 (1995). c) A. Domingo, J. Marcalo, A. Paulo, A. P. de Matos, and I. Santos, *Inorg. Chem.*, **32**, 5114 (1993). d) H. Sugimoto and Y. Sasaki, *Chem. Lett.*, **1997**, 541.

11 **2**: Anal. Calcd for $C_{29}H_{28}Cl_2N_6O_{12}Re_2\cdot CH_3CN\cdot H_2O$: C, 31.37; H, 2.80; N, 8.26%. Found: C, 31.47; H, 2.76; N, 8.34%. ^1H NMR (270 MHz, CD_3CN) δ 8.96 (2H, d, ReO_3-py α-H), 8.88 (2H, d, $Re(CO)_3$-py α-H), 8.28 (2H, t, ReO_3-py γ-H), 8.04 (2H, t, $Re(CO)_3$-py γ-H), 7.73 (4H, q, ReO_3-py β-H and δ-H), 7.63 (2H, d, $Re(CO)_3$-py δ-H), 7.46 (2H, t, $Re(CO)_3$-py β-H), 5.40 (4H, q, ReO_3-pyCH_2N), 5.28 (4H, q, $Re(CO)_3$-pyCH_2N), 4.56 (4H, m, NCH_2CH_2N). UV-vis (CH_3CN) λ_{max}/nm (ε/$M^{-1}\ cm^{-1}$): 302 (sh, 6900), 261 (sh, 18 000), 236 (23 300).

12 D. J. Stufkens, *Comments Inorg. Chem.*, **13**, 359 (1992).

13 L. Duelund, R. Hazell, C. J. McKenzie, L. P. Nielsen, and H. Toftlund, *J. Chem. Soc., Dalton Trans.*, **2001**, 152.

14 L. Xu, Y. Sasaki, and M. Abe, *Chem. Lett.*, **1999**, 163.

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