

Electronic Supplementary Information (ESI)

for

**Synthesis and crystal structure of a dinuclear,
monomeric Mn^{II} *p*-semiquinonato complex**

Harutaka Nakamori, Takahiro Matsumoto, Takeshi Yatabe, Ki-Seok Yoon,
Hidetaka Nakai and Seiji Ogo*

*To whom correspondence should be addressed.

E-mail: ogo.seiji.872@m.kyushu-u.ac.jp

A Table of Contents

Experimental	page 1
Fig. S1	page 5
Fig. S2	page 6
Fig. S3	page 7
Fig. S4	page 8
Fig. S5	page 9
Fig. S6	page 10
Fig. S7	page 11
Fig. S8	page 12
Fig. S9	page 13
Fig. S10	page 14
Fig. S11	page 15
Fig. S12	page 16
References	page 17

Experimental

Materials and methods. All experiments were carried out under an N₂ or Ar atmosphere by using standard Schlenk techniques and a glovebox. Acetonitrile was routinely distilled over CaH₂ under an N₂ atmosphere. It was confirmed that the acetonitrile contains a small amount of H₂O. *N,N*-dimethylformamide (DMF) was distilled over CaH₂ under an N₂ atmosphere and methanol was distilled over Mg/I₂ under an N₂ atmosphere. Diethyl ether was distilled over sodium/benzophenone under an N₂ atmosphere. *p*-Hydroquinone was purchased from Sigma Aldrich, ¹⁸O₂ was purchased from SHOKO Co., LTD. and H₂¹⁸O was purchased from TAIYO NIPPON SANSO Co., LTD. These reagents were used without further purification. [Mn^{III,IV}₂(cyclam)₂(μ-O)₂](ClO₄)₃ {**[2]**(ClO₄)₃, cyclam = 1,4,8,11-tetraazacyclotetradecane} was synthesised according to the methods described in the literature.¹

Electrospray ionization mass spectrometry (ESI-MS) data were obtained by a JEOL JMS-T100ESI AccuTOF LC-plus. UV-vis spectra were recorded on a JASCO V-670 UV-Visible-NIR Spectrophotometer at 25 °C (the light pass length is 0.10 cm). X-band ESR spectra were measured by a JEOL JES-FA200 spectrometer at -150 °C. An IR spectrum of a solid compound in a KBr disk was recorded on a Thermo Nicolet NEXUS 8700 FT-IR instrument. An elemental analysis data was obtained by a PerkinElmer 2400II series CHNS/O analyser using Ar as a carrier gas. ¹H NMR spectra were recorded on a JEOL JNM-AL300 spectrometer at 25 °C. GC-MS data of organic compounds and isotope-labelled water were recorded on a SHIMADZU GCMS-QP 2010 and an Agilent 7890C GC coupled to a 5975C MSD. GC-MS data of isotope-labelled dioxygen gas were recorded on a SHIMADZU GCMS-QP 5050.

[Mn^{II,II}₂(cyclam)₂(μ-SQ)₂](ClO₄)₂ {**[1]**(ClO₄)₂, SQ = *p*-semiquinonato}. To [2](ClO₄)₃ (210 mg, 0.250 mmol) in acetonitrile (8.0 mL) was added *p*-hydroquinone (82.0 mg, 0.750 mmol) in acetonitrile (2.0 mL). After the resulting solution was stirred for 30 min, the solvent was evaporated to afford dark blue powders, which were washed by diethyl ether (10.0 mL) to yield dark blue powders of [1](ClO₄)₂ {yield: 96% based on [2](ClO₄)₃}. Anal. Calcd for [1](ClO₄)₂: C₃₂H₅₆N₈O₁₂Cl₂Mn₂: C, 41.52; H, 6.10; N, 12.11. Found: C, 41.89; H, 6.22; N, 12.17.

Quantitative analysis of *p*-benzoquinone from the reduction of 2 by *p*-hydroquinone. To [2](ClO₄)₃ (210 mg, 0.250 mmol) in acetonitrile (8.0 mL) was

added *p*-hydroquinone (68.3 mg, 0.625 mmol) in acetonitrile (2.0 mL). After the resulting solution was stirred for 30 min, the solvent was evaporated to afford dark blue powders, which were washed by diethyl ether (10.0 mL) to yield dark blue powders of [1](ClO₄)₂. The solvent of diethyl ether solution was removed under reduced pressure to afford yellow powers of *p*-benzoquinone {yield: 47% based on [2](ClO₄)₃}, which was characterised by ¹H NMR spectroscopy and GC-MS.

The above quantitative results of **1** and *p*-benzoquinone indicate that 0.5 equivalent of *p*-benzoquinone relative to **1** is formed.

Qualitative analysis of H₂¹⁸O from the reduction of [Mn^{III,IV}₂(cyclam)₂(μ-¹⁸O)₂]³⁺ (double ¹⁸O-labelled **2) by *p*-hydroquinone.** 3 equivalents of *p*-hydroquinone was added into an acetonitrile solution (200 μL) of [double ¹⁸O-labelled **2**](ClO₄)₃ (10 mM) to form **1** together with H₂¹⁸O, to which was added diethyl ether (200 μL) to precipitate dark blue powers. The powders were removed by filtration and the filtrate was analysed by GC-MS to detect H₂¹⁸O.

Reduction of **2 by *p*-hydroquinone to form **1** followed by UV-vis spectroscopy.** 3 equivalents of *p*-hydroquinone was added into an acetonitrile solution (10 mL) of [2](ClO₄)₃ (1.0 mM) to quantitatively form **1**, which was followed by UV-vis spectroscopy.

Oxidation of **1 by O₂ to form **2** followed by ESI-MS and UV-vis spectroscopy.** O₂ (500 μL) was injected into an acetonitrile solution (500 μL) of [1](ClO₄)₂ (1.0 mM) to form **2**, which was followed by ESI-MS and UV-vis spectroscopy.

Quantitative analysis of **2 from the oxidation of **1** by O₂.** O₂ (5.0 mL) was injected into an acetonitrile solution (5.0 mL) of [1](ClO₄)₂ (46.3 mg, 0.050 mmol), which resulted in the colour change of the solution from dark blue to dark green with formation of insoluble precipitates. The precipitates were removed by filtration and solvent of the filtrate was evaporated to afford dark green powders of [2](ClO₄)₃, which were washed by diethyl ether and dried *in vacuo* {yield: 42% based on [1](ClO₄)₂}.

Quantitative analysis of *p*-benzoquinone from the oxidation of **1 by O₂.** O₂ (500 μL) was injected into a CD₃CN solution (500 μL) of [1](ClO₄)₂ (2.00 μmol), which resulted in the colour change of the solution from dark blue to dark green. To the resulting solution was added 1,4-dioxane (2.00 μmol) as an internal standard and then the amount of *p*-benzoquinone was determined by ¹H NMR spectroscopy {yield: 80% based on [1](ClO₄)₂}. *p*-Benzoquinone was also confirmed by GC-MS.

The results of above quantitative analysis of **2** and *p*-benzoquinone indicate that 2 equivalents of *p*-benzoquinone relative to **2** is formed.

Qualitative analysis of H₂¹⁸O from the oxidation of **1 by ¹⁸O₂.** ¹⁸O₂ (500 μL) was injected into an acetonitrile solution (200 μL) of [**1**](ClO₄)₂ (10 mM) to form double ¹⁸O-labelled **2** with H₂¹⁸O, to which was added diethyl ether (200 μL) to precipitate dark green powders. The powders were removed by filtration and the filtrate was analysed by GC-MS to detect H₂¹⁸O.

Crossover experiment involving 50% ¹⁶O₂ and 50% ¹⁸O₂ followed by ESI-MS. 50 % ¹⁶O₂ and 50% ¹⁸O₂ mixed gas (500 μL) was injected into an acetonitrile solution (500 μL) of [**1**](ClO₄)₂ (1.0 mM) to give **2** {Mn^{III,IV}₂(μ-¹⁶O)₂}, single ¹⁸O-labelled **2** {Mn^{III,IV}₂(μ-^{16,18}O)₂} and double ¹⁸O-labelled **2** {Mn^{III,IV}₂(μ-¹⁸O)₂}. The ratio of Mn^{III,IV}₂(μ-¹⁶O)₂ : Mn^{III,IV}₂(μ-^{16,18}O)₂ : Mn^{III,IV}₂(μ-¹⁸O)₂ was determined by ESI-MS.

Kinetic measurement for isotope exchange of oxo ligands of **2 followed by ESI-MS.** Addition of 5000 equivalents of H₂¹⁸O into an acetonitrile solution (1.5 mL) of [**2**](ClO₄)₃ (1.26 mg, 1.5 μmol) at 33 °C under an N₂ atmosphere formed double ¹⁸O-labelled **2** *via* [Mn^{III,IV}₂(cyclam)₂(μ-^{16,18}O)₂]³⁺ (single ¹⁸O-labelled **2**), which was monitored by ESI-MS.

Reaction of Mn^{II}(ClO₄)₂·6H₂O and cyclam with ¹⁸O₂ in acetonitrile/methanol followed by ESI-MS. To Mn^{II}(ClO₄)₂·6H₂O (36.5 mg, 0.145 mmol) in acetonitrile (500 μL) was added cyclam (21.0 mg, 0.105 mmol) in methanol (500 μL). ¹⁸O₂ (5.0 mL) was injected into the resulting mixture, which resulted in formation of insoluble precipitates. The precipitates were removed by filtration and the filtrate was analysed by ESI-MS, which showed formation of **2**, single ¹⁸O-labelled **2** and double ¹⁸O-labelled **2** (Fig. S11a and S12b).

Reaction of Mn^{II}(ClO₄)₂·6H₂O and cyclam with/without ¹⁶O₂ in acetonitrile/methanol as control experiments followed by ESI-MS. To Mn^{II}(ClO₄)₂·6H₂O (36.5 mg, 0.145 mmol) in acetonitrile (500 μL) was added cyclam (21.0 mg, 0.105 mmol) in methanol (500 μL). O₂ (5.0 mL) was injected into the resulting mixture, which resulted in formation of insoluble precipitates. The precipitates were removed by filtration and the filtrate was analysed by ESI-MS, which showed formation of **2** (Fig. S11b and Fig. S12a). Without O₂, no **2** was formed (Fig. S11d,e).

X-ray crystallographic analysis of [1**](BPh₄)₂.** An X-ray quality crystal of [**1**](BPh₄)₂ was obtained from diffusion of diethyl ether into the acetonitrile solution of

[1](ClO₄)₂ containing 2.5 equivalents of NaBPh₄. Measurements were made on a Rigaku/MSK Saturn CCD diffractometer with confocal monochromated Mo-K α radiation ($\lambda = 0.7107 \text{ \AA}$). Data were collected and processed using the CrystalClear program. Calculations were performed using the CrystalStructure crystallographic software package except for refinement, which was performed using SHELXL-97. Crystallographic data for [1](BPh₄)₂ has been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication No. CCDC 1017487. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK {fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk}.

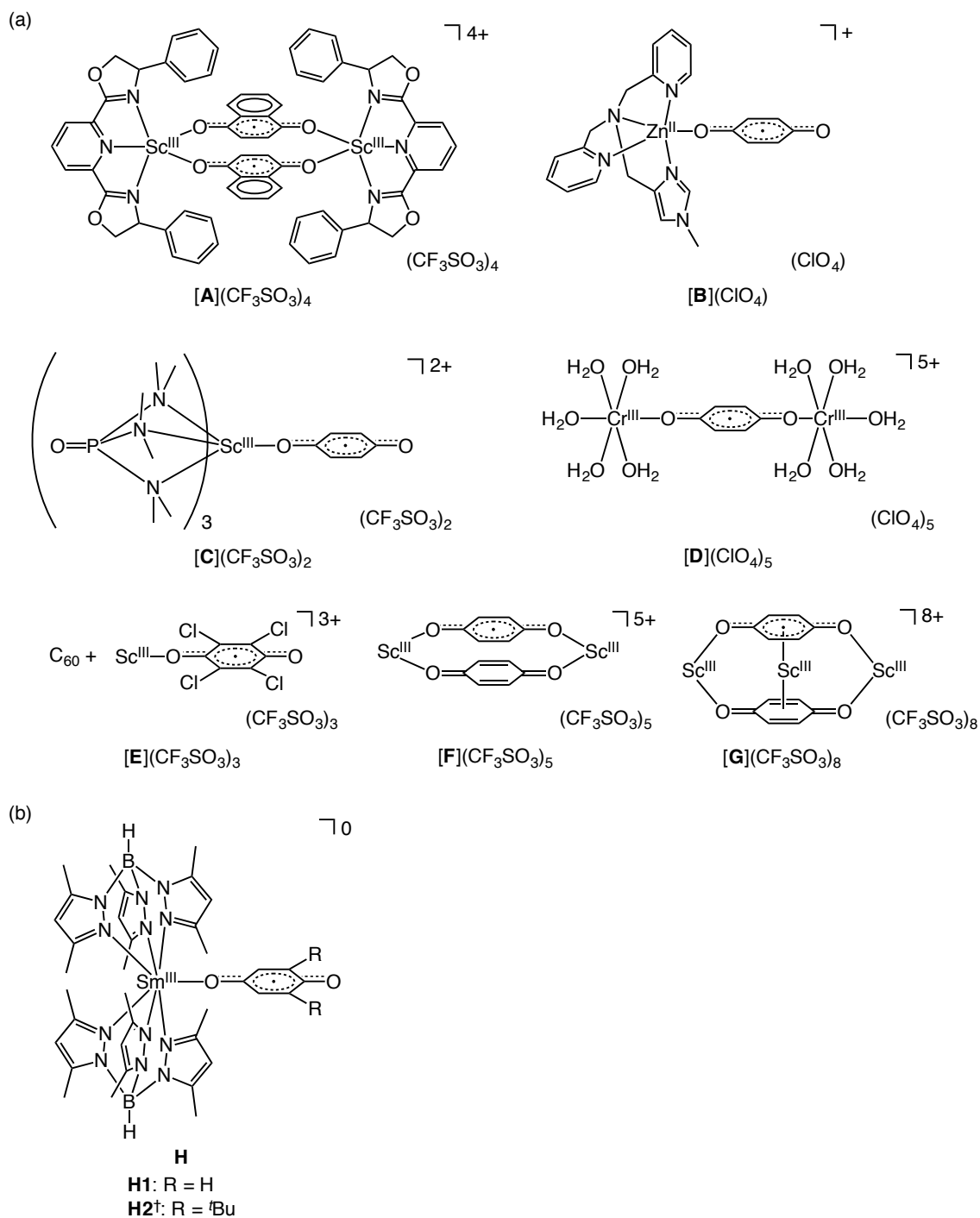


Fig. S1 Monomeric transition metal *p*-semiquinonato complexes **A–H**.^{2–8} (a) *d*-Block metal complexes **A–G**.^{2–7} (b) *f*-Block metal complexes **H**.⁸ †: The structure was determined by X-ray analysis.

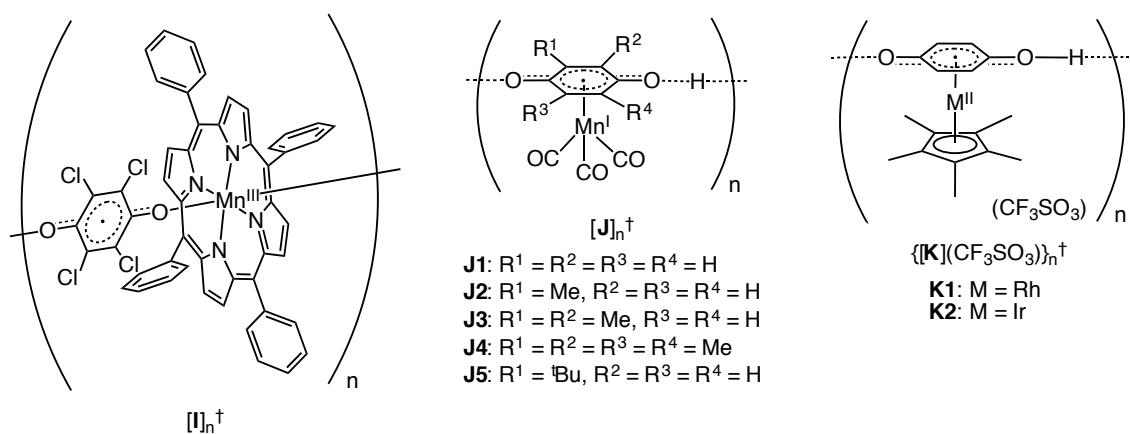


Fig. S2 Polymeric transition metal *p*-semiquinonato complexes **I–K**.^{9–11} †: The structures were determined by X-ray analysis.

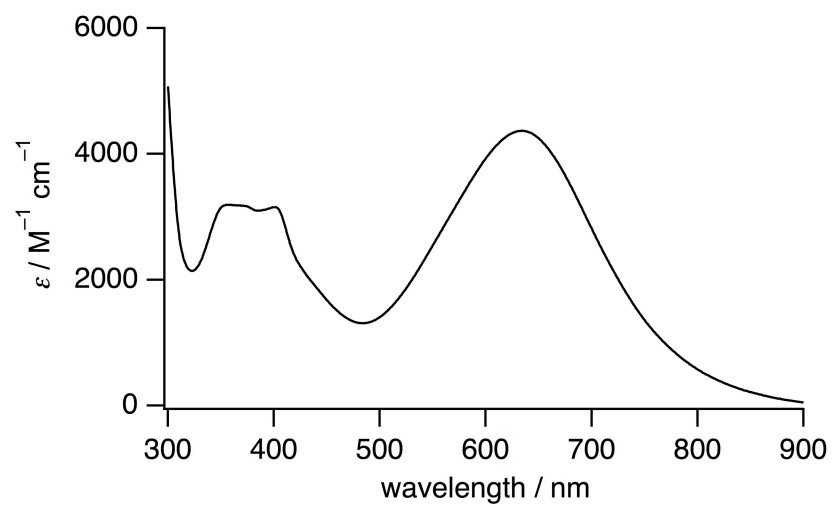


Fig. S3 A UV-vis spectrum of $[\text{Mn}^{\text{II}}_2(\text{cyclam})_2(\mu\text{-SQ})_2](\text{ClO}_4)_2$ $\{[\mathbf{1}](\text{ClO}_4)_2\}$ in acetonitrile under an N_2 atmosphere.

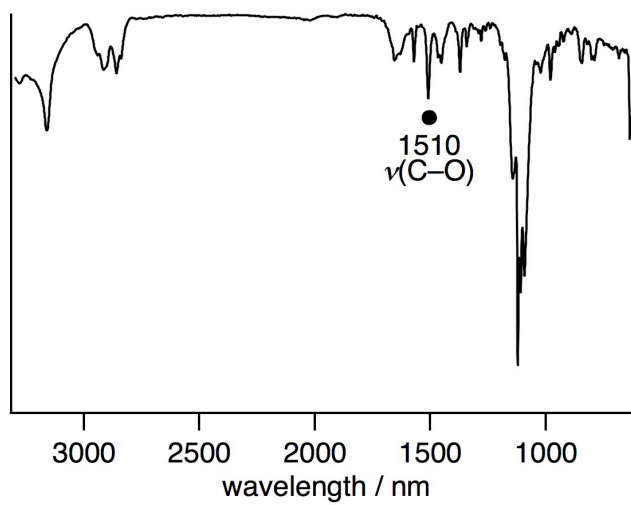


Fig. S4 An IR spectrum of $[\text{Mn}^{\text{II,II}}_2(\text{cyclam})_2(\mu\text{-SQ})_2](\text{ClO}_4)_2$ $\{[\mathbf{1}](\text{ClO}_4)_2\}$ as a KBr disk.

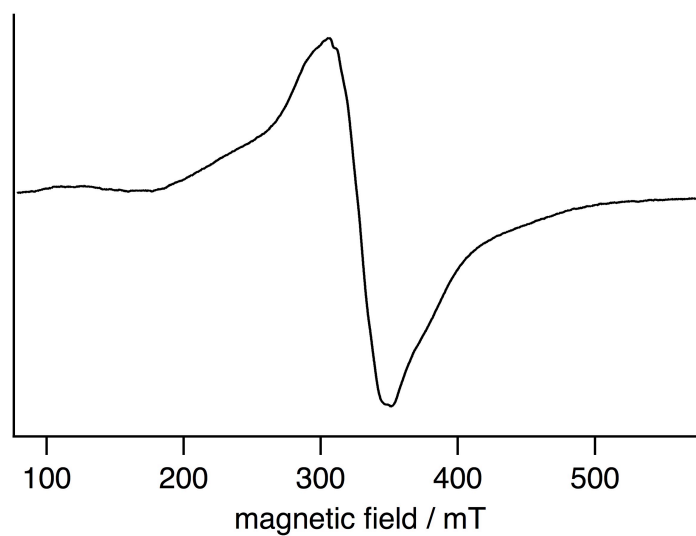


Fig. S5 An ESR spectrum of $[\text{Mn}^{\text{II,II}}_2(\text{cyclam})_2(\mu\text{-SQ})_2](\text{ClO}_4)_2$ $\{[\mathbf{1}](\text{ClO}_4)_2\}$ in frozen DMF at $-150\text{ }^\circ\text{C}$ (microwave frequency: 9.18 GHz, microwave power: 0.25 mW).

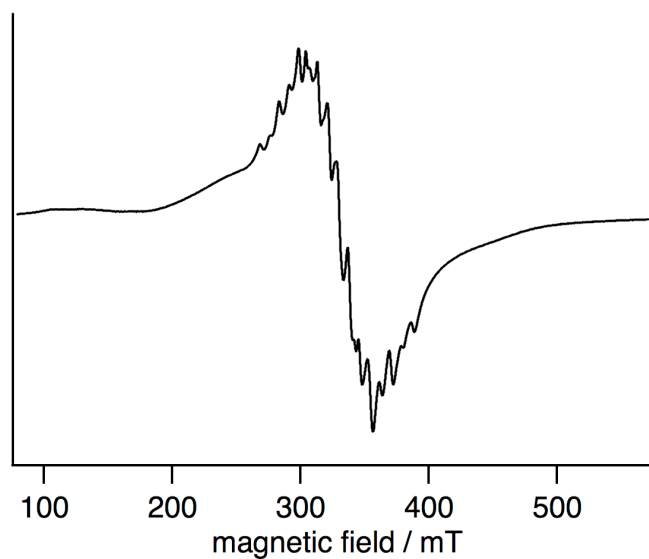


Fig. S6 An ESR spectrum of $[\text{Mn}^{\text{III,IV}}_2(\text{cyclam})_2(\mu\text{-O})_2]^{3+}$ (**2**), obtained from the reaction of **[1]**(ClO₄)₂ with O₂, in frozen DMF at -150 °C (microwave frequency: 9.18 GHz, microwave power: 0.25 mW).

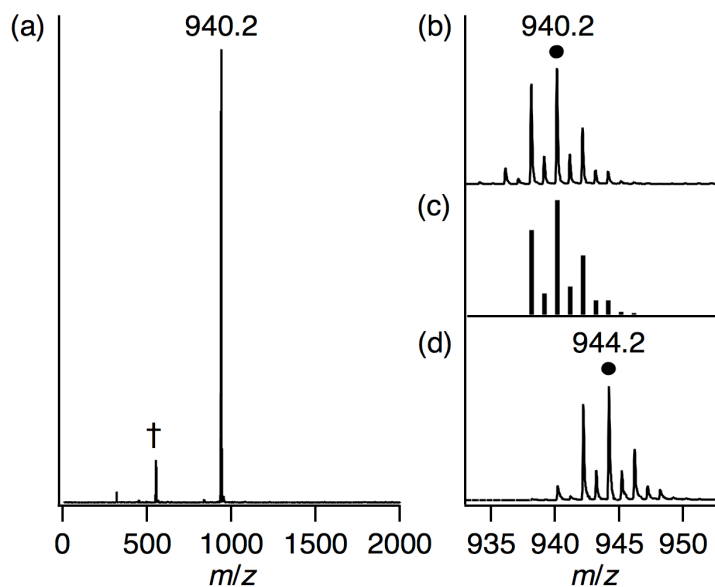


Fig. S7 (a) A negative-ion ESI mass spectrum of $[\text{Mn}^{\text{III,IV}}_2(\text{cyclam})_2(\mu\text{-O})_2]^{3+}$ (**2**) obtained from the reaction of $[\text{Mn}^{\text{II,II}}_2(\text{cyclam})_2(\mu\text{-SQ})_2](\text{ClO}_4)_2$ $\{[\mathbf{1}](\text{ClO}_4)_2\}$ (1.0 mM) with O_2 (500 μL) in acetonitrile (500 μL). †: the signal at 552.0 corresponds to $[\text{Mn}^{\text{II}}(\text{cyclam}) + 3(\text{ClO}_4)]^-$. (b) The signal at 940.2 corresponds to $[\mathbf{2} + 4(\text{ClO}_4)]^-$. (c) Calculated isotopic distribution for $[\mathbf{2} + 4(\text{ClO}_4)]^-$. (d) A negative-ion ESI mass spectrum of $[\text{Mn}^{\text{III,IV}}_2(\text{cyclam})_2(\mu\text{-}^{18}\text{O})_2]^{3+}$ (double ^{18}O -labelled **2**) obtained from the reaction of $[\mathbf{1}](\text{ClO}_4)_2$ (1.0 mM) with $^{18}\text{O}_2$ (500 μL) in acetonitrile (500 μL). The signal at 944.2 corresponds to $[\text{double } ^{18}\text{O}\text{-labelled } \mathbf{2} + 4(\text{ClO}_4)]^-$.

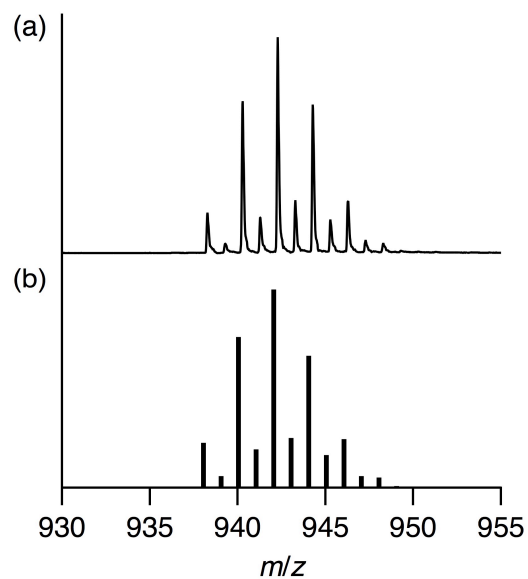


Fig. S8 (a) A negative-ion ESI mass spectrum obtained from the reaction of $[\text{Mn}^{\text{II,II}}_2(\text{cyclam})_2(\mu\text{-SQ})_2](\text{ClO}_4)_2$ $\{[\mathbf{1}](\text{ClO}_4)_2\}$ (10 mM) with 50% $^{16}\text{O}_2$ and 50% $^{18}\text{O}_2$ (500 μL) in acetonitrile (200 μL). (b) Calculated isotopic distribution for combination of $\{[\text{Mn}^{\text{III,IV}}_2(\text{cyclam})_2(\mu\text{-}^{16}\text{O})_2] + 4(\text{ClO}_4)\}^-$, $\{[\text{Mn}^{\text{III,IV}}_2(\text{cyclam})_2(\mu\text{-}^{16,18}\text{O})_2] + 4(\text{ClO}_4)\}^-$ and $\{[\text{Mn}^{\text{III,IV}}_2(\text{cyclam})_2(\mu\text{-}^{18}\text{O})_2] + 4(\text{ClO}_4)\}^-$ at the ratio of 1:2:1.

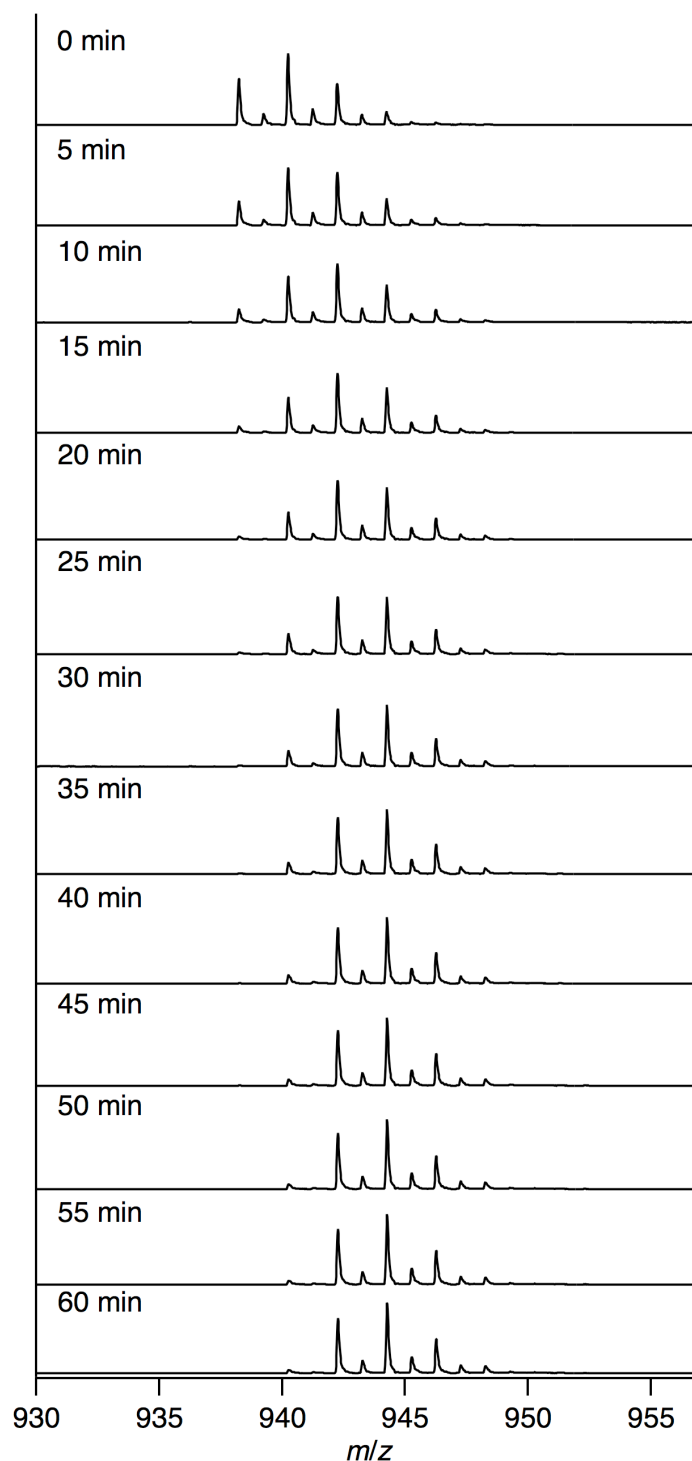


Fig. S9 Negative-ion ESI mass spectral changes from $[\mathbf{2} + 4(\text{ClO}_4)]^-$ (m/z 940.2) to $[\text{double } ^{18}\text{O}\text{-labelled } \mathbf{2} + 4(\text{ClO}_4)]^-$ (m/z 944.2) via $[\text{single } ^{18}\text{O}\text{-labelled } \mathbf{2} + 4(\text{ClO}_4)]^-$ (m/z 942.2) in acetonitrile solution (1.5 mL) containing $\mathbf{2}$ (1.0 mM) with 5000 equivalents of H_2^{18}O (150 μL) at 33 $^\circ\text{C}$. Interval is 5 min. The detailed procedure is described in Experimental.

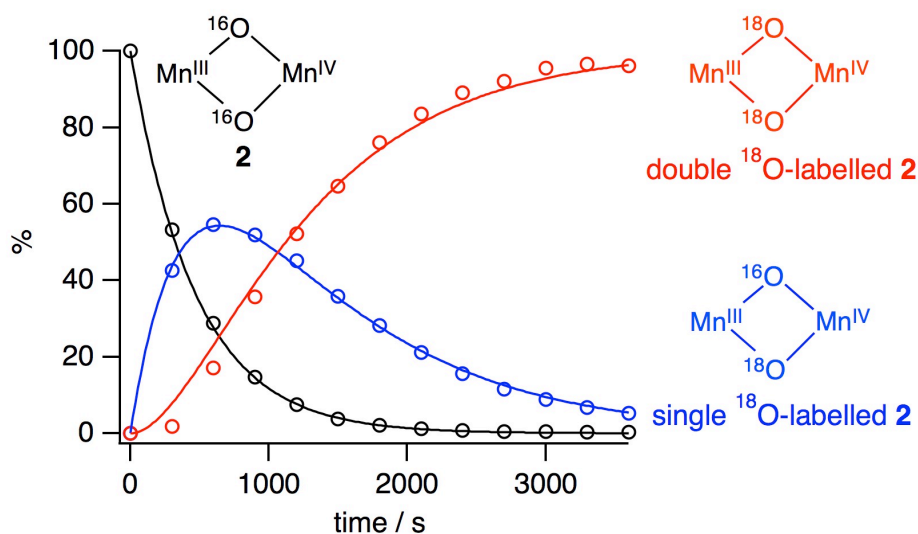
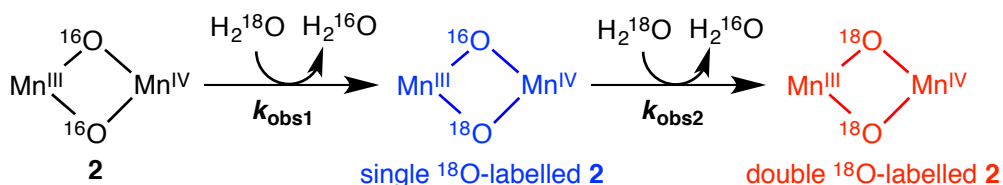


Fig. S10 Time profiles of negative-ion ESI mass spectral signals m/z 938.2 of **2**, m/z 940.2 of single ^{18}O -labelled **2** and m/z 942.2 of double ^{18}O -labelled **2** based on the data from Fig. S9. The lines were fitted by a successive rate equation as follows. The observed rate constants, k_{obs1} and k_{obs2} , were determined as 2.1×10^{-3} and $9.5 \times 10^{-4} \text{ s}^{-1}$, respectively. It is reasonable that the observed rate constant k_{obs2} is a half of k_{obs1} because exchange of ^{18}O ligand of single ^{18}O -labelled **2** for H_2^{18}O also occurs.



$$d[\mathbf{2}]/dt = -k_{\text{obs1}}[\mathbf{2}]$$

$$d[\text{single } ^{18}\text{O}\text{-labelled } \mathbf{2}]/dt = k_{\text{obs1}}[\mathbf{2}] - k_{\text{obs2}}[\text{single } ^{18}\text{O}\text{-labelled } \mathbf{2}]$$

$$d[\text{double } ^{18}\text{O}\text{-labelled } \mathbf{2}]/dt = k_{\text{obs2}}[\text{single } ^{18}\text{O}\text{-labelled } \mathbf{2}]$$

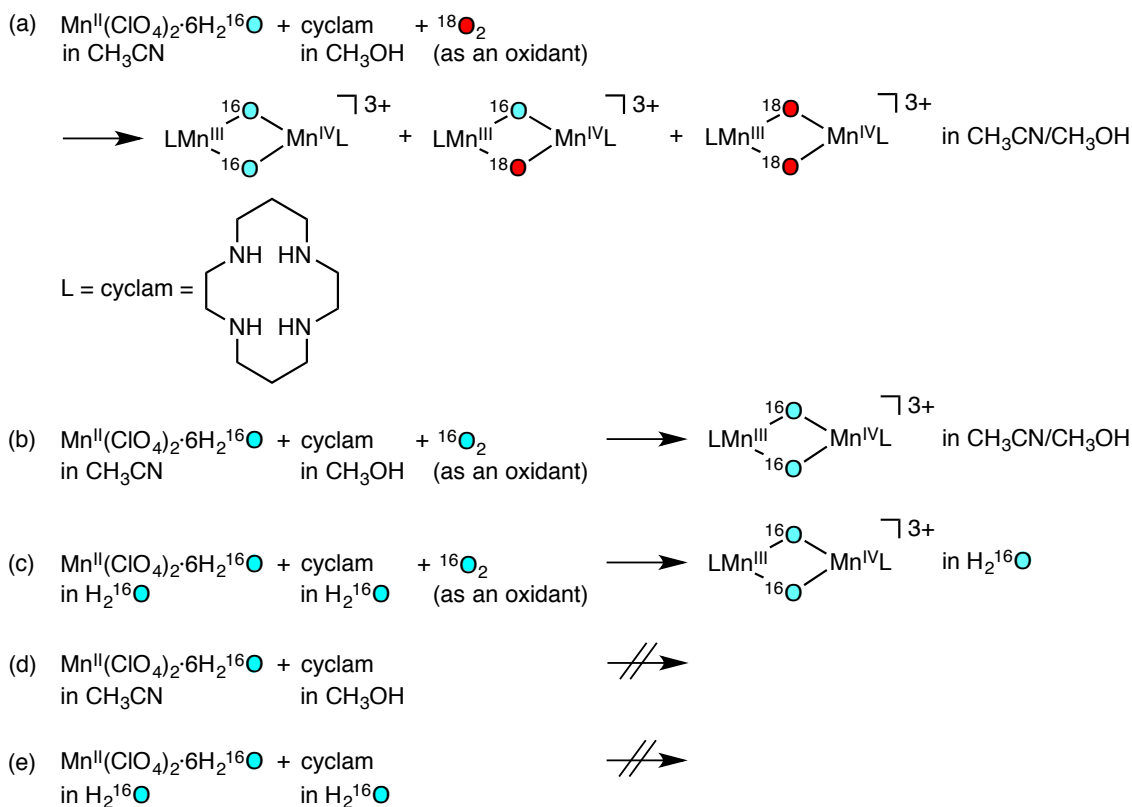


Fig. S11 Reaction of $\text{Mn}^{\text{II}}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and cyclam with/without $^{16}\text{O}_2/^{18}\text{O}_2$ in water/acetonitrile/methanol. (a) See Fig. S12. The ratio of ^{16}O to ^{18}O is ca. 2 to 1. (b)–(e) Control experiments. (b) See Fig. S12. (c) See ref. 1 reported by Calvin et al.

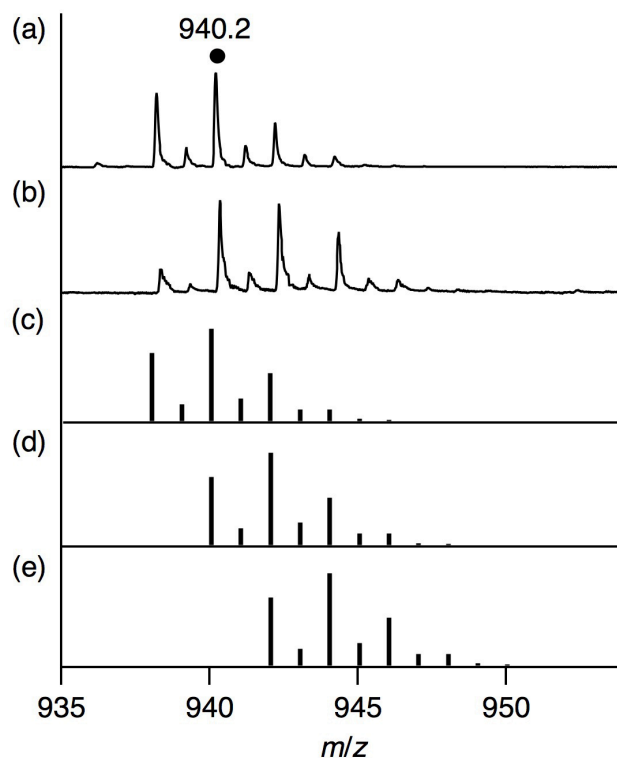


Fig. S12 (a) A negative-ion ESI mass spectrum of $[\text{Mn}^{\text{III,IV}}_2(\text{cyclam})_2(\mu\text{-O})_2]^{3+}$ (**2**), obtained from the reaction of $\text{Mn}^{\text{II}}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and cyclam with $^{16}\text{O}_2$ in acetonitrile/methanol. The signal at 940.2 corresponds to $[\mathbf{2} + 4(\text{ClO}_4)]^-$. (b) A negative-ion ESI mass spectrum obtained from the reaction of $\text{Mn}^{\text{II}}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and cyclam with $^{18}\text{O}_2$ in acetonitrile/methanol, which indicates the mixture of **2**, $[\text{Mn}^{\text{III,IV}}_2(\text{cyclam})_2(\mu\text{-}^{16,18}\text{O})_2]^{3+}$ (single ^{18}O -labelled **2**) and $[\text{Mn}^{\text{III,IV}}_2(\text{cyclam})_2(\mu\text{-}^{18}\text{O})_2]^{3+}$ (double ^{18}O -labelled **2**). The ratio of ^{16}O to ^{18}O is ca. 2 to 1 on the basis of its isotopic distribution. The detailed procedures are described in Experimental. (c) Calculated isotopic distribution for $[\mathbf{2} + 4(\text{ClO}_4)]^-$. (d) Calculated isotopic distribution for $[\text{single } ^{18}\text{O}\text{-labelled } \mathbf{2} + 4(\text{ClO}_4)]^-$. (e) Calculated isotopic distribution for $[\text{double } ^{18}\text{O}\text{-labelled } \mathbf{2} + 4(\text{ClO}_4)]^-$.

References

1. K. J. Brewer, M. Calvin, R. S. Lumpkin, J. W. Otvos and L. O. Spreer, *Inorg. Chem.*, 1989, **28**, 4446–4451.
2. J. Yuasa and S. Fukuzumi, *J. Am. Chem. Soc.*, 2007, **129**, 12912–12913.
3. H. Ohtsu and S. Fukuzumi, *Angew. Chem. Int. Ed.*, 2000, **39**, 4537–4539.
4. T. Kawashima, K. Ohkubo and S. Fukuzumi, *Phys. Chem. Chem. Phys.*, 2011, **13**, 3344–3352.
5. S. L. Scott, A. Bakac and J. H. Espenson, *J. Am. Chem. Soc.*, 1992, **114**, 4605–4610.
6. S. Fukuzumi, H. Mori, H. Imahori, T. Suenobu, Y. Araki, O. Ito and K. M. Kadish, *J. Am. Chem. Soc.*, 2001, **123**, 12458–12465.
7. J. Yuasa, T. Suenobu and S. Fukuzumi, *J. Am. Chem. Soc.*, 2003, **125**, 12090–12091.
8. Â. Domingos, I. Lopes, J. C. Waerenborgh, N. Marques, G. Y. Lin, X. W. Zhang, J. Takats, R. McDonald, A. C. Hillier, A. Sella, M. R. J. Elsegood and V. W. Day, *Inorg. Chem.*, 2007, **46**, 9415–9424.
9. E. J. Brandon, R. D. Rogers, B. M. Burkhardt and J. S. Miller, *Chem. Eur. J.*, 1998, **4**, 1938–1943.
10. M. Oh, J. A. Reingold, G. B. Carpenter and D. A. Sweigart, *J. Organomet. Chem.*, 2003, **687**, 78–84.
11. J. Moussa, C. Guyard-Duhayon, P. Herson, H. Amouri, M. N. Rager and A. Jutand, *Organometallics*, 2004, **23**, 6231–6328.