

Isolation of Enantiopure Crystals and Spectroscopic Properties of a Chiral Er-Containing Polyoxotungstate $[\text{Er}(\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61})_2]^{17-}$

Jun Iijima, Haruo Naruke,* and Takano Sanji

Chemical Resources Laboratory, Tokyo Institute of Technology,
4259-R1-23 Nagatsuta, Midori-ku, Yokohama, Kanagawa 226-8503

(Received November 5, 2011; CL-111080; E-mail: hnaruke@res.titech.ac.jp)

Enantiopure crystals of chiral $[\text{L-}/\text{D-Er}(\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61})_2]^{17-}$ polyanions were successfully resolved by using L-/D-proline (pro) as chiral auxiliaries. In both crystals, the chirality was stabilized by enantioselective interaction involving N–H...O hydrogen bonding between the polyanion and pro molecules. Circular dichroic spectroscopy in aqueous solutions revealed that partial racemization of the polyanions and the racemic equilibrium can be enantioselectively controlled by the amount of coexisting pro.

Chiral polyoxometalates (POMs) have received much attention for a long time owing to not only a broad spectrum of application such as nonlinear optics, asymmetric catalysis, and inorganic medicine but also their distinctive structure and geometric topology.¹ However, most of the reported chiral POMs are known to racemize in solutions as well as in the solid state because of their partial hydrolysis and fluxional behavior.² In a great number of chiral POMs, there are a few examples of the enantiomerically isolated chiral POMs by means of spontaneous resolution and optical resolution.

After the first discovery of the spontaneous resolution of NH_4^+ salt of $[\text{MnMo}_9\text{O}_{32}]^{6-}$ by Pauling in 1954,³ wide-ranging POMs with chiral space groups have been reported to date. But, the synthesis of chiral POMs utilizing spontaneous resolution is not useful for further application since the overall products are enantiomixtures.

As for the optical resolution, $[\text{H}_4\text{Co}_2\text{Mo}_{10}\text{O}_{36}]^{6-}$ was reported by Ama et al. in 1970 to be the first example,⁴ which was resolved by using a chiral $[\text{Co}(\text{en})_3]^+$ complex. Recently, studies of enantiomeric separation of $[\text{P}_2\text{Mo}_{18}\text{O}_{62}]^{6-}$ with amino acids such as lysine and histidine were conducted by the Wang group.⁵ These methods produce enantiopure POMs and therefore, are more practical than spontaneous resolution.

Chiral C_2 -symmetric sandwich-type $[\text{Ln}(\alpha\text{-XM}_{11}\text{O}_{39})_2]^{n-}$ and $[\text{Ln}(\alpha_2\text{-X}_2\text{M}_{17}\text{O}_{61})_2]^{n-}$, first reported by Peacock and Weakley,⁶ have the central Ln coordinated by two mono-lacunary Keggin $[\alpha\text{-XM}_{11}\text{O}_{39}]^{n-}$ and Wells–Dawson $[\alpha_2\text{-X}_2\text{M}_{17}\text{O}_{61}]^{n-}$ ligands with a square-antiprism geometry. The relative twist between the mono-lacunary units resulting from the square-antiprismatic coordination to Ln gives rise to the molecular chirality and defines a pair of two enantiomers. In most cases, $[\text{Ln}(\alpha\text{-XM}_{11}\text{O}_{39})_2]^{n-}$ and $[\text{Ln}(\alpha_2\text{-X}_2\text{M}_{17}\text{O}_{61})_2]^{n-}$ polyanions racemize in solutions and crystallize as racemic solids. Meanwhile, for the last several years, dimethylammonium salts of $[\text{M}^{\text{IV}}(\alpha\text{-PW}_{11}\text{O}_{39})_2]^{10-}$ ($\text{M} = \text{Hf}^{\text{IV}}$, Zr^{IV} , and Ce^{IV}) polyanions have been continuously delivered as new examples that were spontaneously resolved.⁷

Recently, our group has reported an enantioselective synthesis of $[\text{Ln}(\alpha\text{-PW}_{11}\text{O}_{39})_2]^{11-}$ using a proline (pro: $\text{HNC}_4\text{H}_7\text{COOH}$) molecule as chiral auxiliary for the first time.⁸ L- and D-Pro have been used for diastereomeric recognition of a Ln^{3+} : $[\alpha_1\text{-P}_2\text{W}_{17}\text{O}_{61}]^{10-} = 1:1$ type $[\text{Ln}^{\text{III}}(\alpha_1\text{-P}_2\text{W}_{17}\text{O}_{61})(\text{H}_2\text{O})_n]^{7-}$ polyan-

ion, evidenced by ^{31}P and ^{183}W NMR spectroscopy.⁹ Herein, we report the first enantioselective isolation of $[\text{Er}(\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61})_2]^{17-}$ polyanion using L- and D-pro. The chirality of this anion in aqueous solution and in the solid state was confirmed by means of circular dichroic (CD) spectroscopy and single crystal X-ray diffraction analysis.

The enantiopure crystals of $\text{K}_{14}\text{H}_3[\text{L-Er}(\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61})_2] \cdot 2(\text{L-pro}) \cdot 44\text{H}_2\text{O}$ (**Er-L-Dawson**) and $\text{K}_{14}\text{H}_3[\text{D-Er}(\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61})_2] \cdot 2(\text{D-pro}) \cdot 41\text{H}_2\text{O}$ (**Er-D-Dawson**) were obtained by using a modified procedure for enantioselective isolation of Na^+/K^+ -mixed salts of $[\text{Ln}(\alpha\text{-PW}_{11}\text{O}_{39})_2]^{11-}$ in the literature.⁸ To a solution of KCl (0.15 g, 2.0 mmol) in 20 mL of H_2O were added both solid L-pro (0.58 g, 5.0 mmol) and $\text{ErCl}_3 \cdot 6\text{H}_2\text{O}$ (0.38 g, 1.0 mmol) dissolved in 5 mL of H_2O . The clear solution was heated at 60 °C for 30 min with stirring. The solution was then acidified with 1 M HCl to pH 1.5 and an aqueous solution (20 mL) of $\text{K}_6[\text{P}_2\text{W}_{18}\text{O}_{62}] \cdot 6\text{H}_2\text{O}$ (9.2 g, 2.0 mmol)¹⁰ was added dropwise. After adjusting the pH to ca. 5 by addition of solid Li_2CO_3 , the solution was boiled for 1 h and cooled to room temperature. The residual powders were filtered off, and the resulting filtrate was concentrated to less than half of the initial volume and stood at room temperature for several days. Light pink block crystals of **Er-L-Dawson** were obtained (yield; 3.43 g, 34.4% based on W). The use of D-pro as a chiral source instead of L-pro yielded crystals of **Er-D-Dawson** (yield; 1.14 g, 11.4% based on W).

From single crystal X-ray diffraction analysis,¹¹ the two crystals are isomorphous with a space group $P2_12_12$. The asymmetric unit is composed of a $[\text{Er}(\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61})_2]^{17-}$ polyanion, 14K^+ ions, two L- or D-pro, and some waters of crystallization. Their chemical formulas are consistent with the results of CHN elemental analysis¹³ and TG-DTA (Figure S1¹⁹). It is of significance that the unique polyanion enantiomer $[\text{L-}/\text{D-Er}(\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61})_2]^{17-}$ was selectively isolated by the use of L- or D-pro, respectively. The reasonably small Flack parameters¹⁴ of 0.010(8) for **Er-L-Dawson** and 0.015(9) for **Er-D-Dawson** support the chirality of these crystals.

The polyanion is composed of two mono-lacunary Wells–Dawson $[\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61}]^{10-}$ units coordinating to Er^{3+} with a square-antiprism geometry (Figure 1). The Er^{3+} center is positioned on the crystallographic C_2 axis parallel to the c axis. Therefore, the polyanion has an ideal C_2 point symmetry in the crystal. The pK_a (1.95 and 10.47) of pro¹⁵ and the weakly acidic condition (pH 5) in the synthetic procedure suggest that all the pro molecules are zwitterionic. In fact, the carboxylate group coordinating to a K^+ cation (Figure S2¹⁹) has two similar (1.24(2)–1.29(3) Å) C–O distances due to a resonance state.

The two pro molecules are located in the proximity of Er^{3+} , and distances from the amino-N atoms in pro to O atoms coordinating to Er^{3+} are 2.847(14) and 3.021(13) Å for **Er-L-Dawson** and 2.806(15) and 3.008(14) Å for **Er-D-Dawson**, suggesting the presence of N–H...O hydrogen bondings between $[\text{L-}/\text{D-Er}(\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61})_2]^{17-}$ and L-/D-pro. We have reported

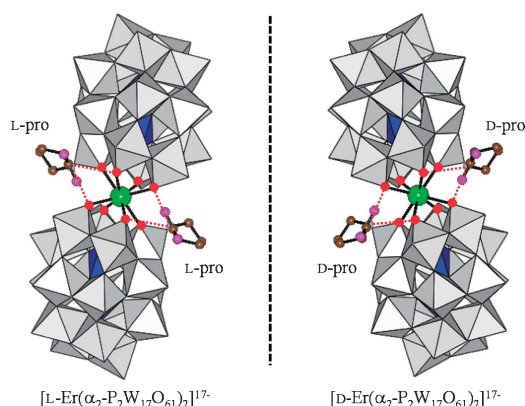


Figure 1. Combined polyhedral and ball-and-stick model of $[L\text{-}/D\text{-Er}(\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61})_2]^{17-}$ polyanions hydrogen-bonded by *L*-/*D*-pro molecules in **Er-L-Dawson** (left) and **Er-D-Dawson** (right) viewed along the molecular C_2 axes. The N...O hydrogen bondings are emphasized with red dotted line. Color codes; white octahedron: WO_6 , blue tetrahedron: PO_4 , green sphere: Er, pink sphere: carboxy O in pro, red sphere: O coordinating to Er, brown sphere: C, light blue sphere: N.

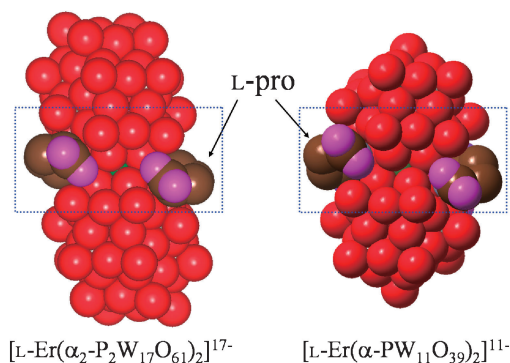


Figure 2. Space-filling model of polyanions and *L*-pro in **Er-L-Dawson** (left) and **Er-L-Keggin** (right). The isostructural areas around the Er centers are highlighted by the blue dotted rectangles. Color codes of spheres; red: O in the polyanion, dark green: Er, pink: carboxylate O in pro, light blue: N, brown: C.

similar hydrogen-bonding interaction and molecular association between $[\text{Ln}(\alpha\text{-PW}_{11}\text{O}_{39})_2]^{11-}$ ($\text{Ln} = \text{Pr}$ and Er) and pro in enantiopure $\text{K}_{1.3}\text{Na}_{3.2}\text{H}_{6.5}[\text{L-Er}(\alpha\text{-PW}_{11}\text{O}_{39})_2] \cdot 8.3(\text{L-pro}) \cdot 22.5\text{H}_2\text{O}$ (**Er-L-Keggin**) and $\text{K}_{1.3}\text{Na}_{3.2}\text{H}_{6.5}[\text{D-Er}(\alpha\text{-PW}_{11}\text{O}_{39})_2] \cdot 8.3(\text{D-pro}) \cdot 14\text{H}_2\text{O}$ (**Er-D-Keggin**) crystals.⁸ The similarity is due to the isostructural polyanion frameworks around the Ln^{3+} centers (Figure 2). Thus, it is strongly suggested that stereo-specific and -selective interactions between the polyanion and pro, stabilize the square-antiprism coordination of Er^{3+} and contribute to the selective isolation of **Er-L/D-Dawson**.

The IR spectrum of **Er-L-Dawson** (Figure 3) contains stretching bands of $\nu(\text{P-O})$ (1084, 1056, 1027, and 1015 cm^{-1}), $\nu(\text{W-O}_i)$ (940 cm^{-1}), $\nu(\text{W-O}_b\text{-W})$ (916, 888, and 826 cm^{-1}), and $\nu(\text{W-O}_c\text{-W})$ (777 and 729 cm^{-1}).¹⁶ These band energies are close to those for the K salt of $[\text{Yb}(\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61})_2]^{17-}$,¹⁷ showing little effect of counter cation and Ln^{3+} species. The weak bands around $1420\text{--}1250\text{ cm}^{-1}$ are due to the pyrrolidine ring of pro in crystals. The spectrum of **Er-D-Dawson** is identical with that of **Er-L-Dawson** (Figure S3¹⁹).

Figure 4 shows the ^{31}P NMR spectrum of **Er-L-Dawson** in D_2O solution. A pair of two major resonance peaks is observed.

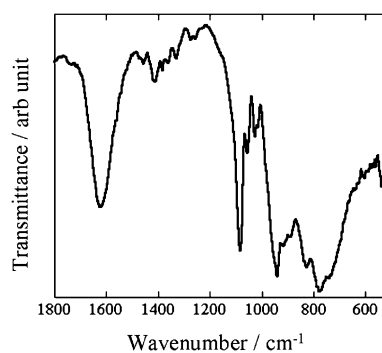


Figure 3. The IR spectrum of **Er-L-Dawson**.

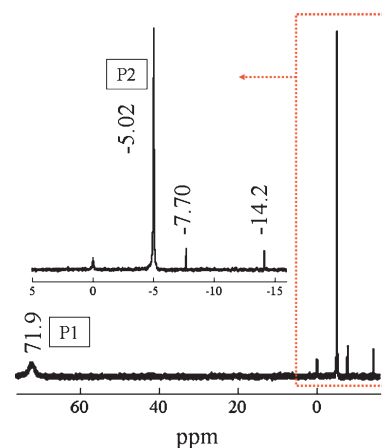


Figure 4. The ^{31}P NMR spectrum of **Er-L-Dawson** in D_2O solution (20.1 mM). The inset is a magnified spectrum of the orange rectangled region.

Referring to the previous study of $[\text{Er}(\alpha\text{-PW}_{11}\text{O}_{39})_2]^{11-}$ by Fedotov et al.,¹⁸ one broadened peak at 71.9 ppm is assignable to the P1 atom close to Er^{3+} , and another peak at -5.02 ppm to the P2 atom far from Er^{3+} . The large positive shift and broadened peak for P1 is ascribable to a paramagnetic effect of Er^{3+} .¹⁸ A couple of minor peaks (less than 5% to $[\text{Er}(\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61})_2]^{17-}$) at -7.70 and -14.2 ppm are attributable to a free $[\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61}]^{10-}$ moiety,¹⁰ indicating that $[\text{Er}(\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61})_2]^{17-}$ is stable in aqueous solution. As expected, the spectrum of **Er-D-Dawson** is identical to that of **Er-L-Dawson** (Figure S4¹⁹).

The CD spectra of **Er-L/D-Dawson** in aqueous solutions are shown with blue solid and broken plots in Figure 5 ($400\text{--}550\text{ nm}$; magnified spectra: Figure S6a¹⁹) and in Figure S7¹⁹ ($375\text{--}420\text{ nm}$). The spectra in the former and latter regions are assignable to the $f \rightarrow f$ transitions in Er^{3+} (absorption spectrum: Figure S6b¹⁹) and $\text{O} \rightarrow \text{W}$ charge-transfer (CT) bands in the $[\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61}]^{10-}$ units, respectively. These mirror-imaged CD spectra reveal the presence of the $[L\text{-}/D\text{-Er}(\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61})_2]^{17-}$ enantiomers in solutions. Although the signs of ellipticities for the $f \rightarrow f$ transitions are consistent with those for **Er-L/D-Keggin**⁸ (Figure S6c¹⁹), their overall CD signals are weak under the comparable polyanion concentrations. Note that a partial racemization occurs in the **Er-L/D-Keggin** solutions, and the resulting racemic equilibrium is shifted to either of the enantiomers by interaction with coexistent *L*-/*D*-pro.⁸ Assuming a similar behavior in the **Er-L/D-Dawson** solutions, the weak CD signals are attributable to the smaller pro/polyanion molar ratio (= 2) in **Er-L/D-Dawson** than that (= 8.3)

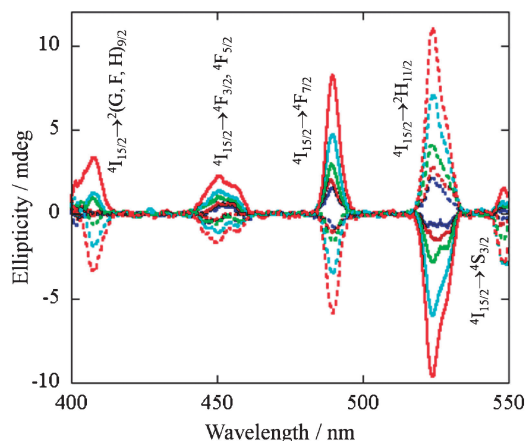


Figure 5. The variations of CD spectra of the aqueous **Er-L-Dawson** (solid) and **Er-D-Dawson** (dotted) solutions (30 mM) by addition of L- and D-pro, respectively. The assignments are due to f-f transitions of Er^{3+} . The pro/polyanion molar ratio in solutions: 2 (blue, before addition), 4 (red), 8 (green), 16 (light blue), 32 (orange).

in **Er-L/D-Keggin**. To confirm this, the CD spectra were measured for the **Er-L/D-Dawson** solutions to which extra L- and D-pro were added successively. For both solutions, an increase of the pro/polyanion molar ratio from 2 to 32 gives rise to a remarkable enhancement of ellipticities of the $f \rightarrow f$ (Figure 5) and $O \rightarrow W$ CT (Figure S7¹⁹) bands. This result demonstrates that dissolution of the **Er-L/D-Dawson** crystals to water results in a rapid racemization to establish an equilibrium between $[\text{L-Er}(\alpha_2\text{-P}_2\text{-W}_{17}\text{O}_{61})_2]^{17-}$ and $[\text{D-Er}(\alpha_2\text{-P}_2\text{-W}_{17}\text{O}_{61})_2]^{17-}$, and the equilibrium is shifted by the coexisting L- and D-pro.

Plots of the CD intensity vs. pro/polyanion ratio (from Figures 5 and S7¹⁹) exhibit an approximate linear increase of ellipticities (Figure S8¹⁹), suggesting that polyanion-pro complexation or interaction is weak in aqueous solutions. This is supported by the observation of only two ^{31}P NMR peaks for the polyanion (Figure 4)²⁰ and no peak-splitting caused by diastereomeric interaction between the polyanion and pro.^{9a} Further addition of L-pro to the **Er-L-Dawson** solution had no effect on the ^{31}P NMR peaks of the polyanion (Figure S5¹⁹).

In conclusion, we have obtained the enantiopure crystals of **Er-L-Dawson** and **Er-D-Dawson**. The stereospecific hydrogen-bonding interaction between $[\text{Er}(\alpha_2\text{-P}_2\text{-W}_{17}\text{O}_{61})_2]^{17-}$ and pro stabilizes the chirality in the solid state. In the aqueous solutions, the CD signals of the chiral polyanions due to the Er^{3+} : $f \rightarrow f$ and $O \rightarrow W$ CT transitions are weak because of the partial racemization, but the equilibrium balance between the two enantiomers is effectively controllable by the coexisting L-/D-pro added to the solutions. The knowledge obtained in this study may open the way for not only resolution methods for chiral POMs by organic molecules but also their future application.

References and Notes

1 a) B. Hasenknopf, K. Micoine, E. Lacôte, S. Thorimbert, M. Malacria, R. Thouvenot, *Eur. J. Inorg. Chem.* **2008**, 5001. b) K. Micoine, B. Hasenknopf, S. Thorimbert, E. Lacôte, M. Malacria, *Angew. Chem., Int. Ed.* **2009**, *48*, 3466. c) M. Inoue, T. Yamase, *Bull. Chem. Soc. Jpn.* **1995**, *68*, 3055. d) M. Inoue, T. Yamase, *Bull. Chem. Soc. Jpn.* **1996**, *69*, 2863. e) H.-Y. An, E.-B. Wang, D.-R. Xiao, Y.-G. Li, Z.-M. Su, L. Xu, *Angew. Chem., Int. Ed.* **2006**, *45*, 904. f) Y.-Q. Lan, S.-L. Li, Z.-M. Su, K.-Z. Shao, J.-F. Ma, X.-L. Wang, E.-B. Wang, *Chem. Commun.*

- 2008**, *58*. g) Y.-Q. Lan, S.-L. Li, X.-L. Wang, K.-Z. Shao, D.-Y. Du, Z.-M. Su, E.-B. Wang, *Chem.—Eur. J.* **2008**, *14*, 9999.
- 2 a) R. Strandberg, *Acta Chem. Scand.* **1973**, *27*, 1004. b) K. Y. Matsumoto, *Bull. Chem. Soc. Jpn.* **1979**, *52*, 3284. c) M. T. Pope, *Inorg. Chem.* **1976**, *15*, 2008. d) H. D'Amour, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1976**, *32*, 729. e) A. Tézé, G. Hervé, *J. Inorg. Nucl. Chem.* **1977**, *39*, 999.
- 3 J. L. T. Waugh, D. P. Shoemaker, L. Pauling, *Acta Crystallogr.* **1954**, *7*, 438.
- 4 T. Ama, J. Hidaka, Y. Shimura, *Bull. Chem. Soc. Jpn.* **1970**, *43*, 2654.
- 5 a) J. Liu, J. Peng, E. Wang, L. Bi, S. Guo, *J. Mol. Struct.* **2000**, *525*, 71. b) D. Liu, H.-Q. Tan, W.-L. Chen, Y.-G. Li, E.-B. Wang, *CrystEngComm* **2010**, *12*, 2044.
- 6 R. D. Peacock, T. J. R. Weakley, *J. Chem. Soc. A* **1971**, 1836.
- 7 a) Y. Hou, X. Fang, C. L. Hill, *Chem.—Eur. J.* **2007**, *13*, 9442. b) L. Cai, Y. Li, C. Yu, H. Ji, Y. Liu, S. Liu, *Inorg. Chim. Acta* **2009**, *362*, 2895. c) J. Iijima, E. Ishikawa, Y. Nakamura, H. Naruke, *Inorg. Chim. Acta* **2010**, *363*, 1500.
- 8 H. Naruke, J. Iijima, T. Sanji, *Inorg. Chem.* **2011**, *50*, 7535.
- 9 a) M. Sadakane, M. H. Dickman, M. T. Pope, *Inorg. Chem.* **2001**, *40*, 2715. b) C. Boglio, B. Hasenknopf, G. Lenoble, P. Rémy, P. Gouzerh, S. Thorimbert, E. Lacôte, M. Malacria, R. Thouvenot, *Chem.—Eur. J.* **2008**, *14*, 1532.
- 10 D. K. Lyon, W. K. Miller, T. Novet, P. J. Dommelle, E. Evitt, D. C. Johnson, R. G. Finke, *J. Am. Chem. Soc.* **1991**, *113*, 7209.
- 11 X-ray diffraction data for both compounds were collected on a Rigaku RAXIS-RAPID imaging plate diffractometer with a graphite monochromatized $\text{MoK}\alpha$ radiation ($\lambda = 0.7107 \text{ \AA}$) at 203 and 193 K, respectively. Crystal data for **Er-L-Dawson**: $\text{O}_{170}\text{ErP}_4\text{W}_{34}\text{K}_{14}\text{C}_{10}\text{N}_2\text{H}_{109}$, fw 10067.31, orthorhombic, space group $P2_12_12_1$, $a = 12.4842(2) \text{ \AA}$, $b = 43.1675(7) \text{ \AA}$, $c = 14.7853(2) \text{ \AA}$, $V = 7967.9(3) \text{ \AA}^3$, $Z = 2$, $D_{\text{calcd}} = 4.196 \text{ g cm}^{-3}$, $\mu = 25.5102 \text{ mm}^{-1}$, $F(000) = 8906.00$, crystal description, $0.49 \times 0.09 \times 0.08 \text{ mm}^3$, platelet, light pink. Of 129264 reflections collected ($3.1^\circ < \theta < 27.5^\circ$), 18256 reflections were unique ($R_{\text{int}} = 0.0566$). $R_1 = 0.0265$ ($I > 2\sigma(I)$) and $wR_2 = 0.0654$ (all data). CCDC-850814. Crystal data for **Er-D-Dawson**: $\text{O}_{167}\text{ErP}_4\text{W}_{34}\text{K}_{14}\text{C}_{10}\text{N}_2\text{H}_{103}$, fw 10013.27, orthorhombic, space group $P2_12_12_1$, $a = 12.4609(2) \text{ \AA}$, $b = 43.1877(7) \text{ \AA}$, $c = 14.7655(2) \text{ \AA}$, $V = 7946.1(2) \text{ \AA}^3$, $Z = 2$, $D_{\text{calcd}} = 4.185 \text{ g cm}^{-3}$, $\mu = 25.5776 \text{ mm}^{-1}$, $F(000) = 8846.00$, crystal description, $0.26 \times 0.12 \times 0.10 \text{ mm}^3$, block, light pink. Of 128366 reflections collected ($3.1^\circ < \theta < 27.6^\circ$), 18206 reflections were unique ($R_{\text{int}} = 0.0845$). $R_1 = 0.0341$ ($I > 2\sigma(I)$) and $wR_2 = 0.0855$ (all data). CCDC-850815. Both structures were solved by the direct method (SHELXS-97^{12a}) and refined by the full-matrix least squares on F^2 using the CrystalStructure.^{12b} The Er, W, P, and K atoms were refined anisotropically. The O atoms in pro were refined anisotropically, while the other O atoms isotropically. The H atoms were not included in the refinements.
- 12 a) G. M. Sheldrick, *SHELXS-97, Program for the Solution of Crystal Structures*, University of Göttingen, Germany, **1997**. b) *CrystalStructure: Crystal Structure Analysis Package*, Rigaku Corporation.
- 13 Anal. Calcd for $\text{O}_{170}\text{ErP}_4\text{W}_{34}\text{K}_{14}\text{C}_{10}\text{N}_2\text{H}_{109}$ (**Er-L-Dawson**): C, 1.19; H, 1.09; N, 0.28; Er, 1.66; P, 1.23; K, 5.44; W, 62.09%. Found: C, 1.18; H, 0.52; N, 0.28; Er, 1.58; P, 1.25; K, 5.98; W, 59.49%. Anal. Calcd for $\text{O}_{167}\text{ErP}_4\text{W}_{34}\text{K}_{14}\text{C}_{10}\text{N}_2\text{H}_{103}$ (**Er-D-Dawson**): C, 1.20; H, 1.04; N, 0.28; Er, 1.67; P, 1.24; K, 5.47; W, 62.43%. Found: C, 0.99; H, 0.69; N, 0.28; Er, 1.60; P, 1.23; K, 5.74; W, 58.93%.
- 14 H. D. Flack, *Acta Crystallogr., Sect. A: Found. Crystallogr.* **1983**, *39*, 876.
- 15 *Handbook of Chemistry and Physics*, 88th ed., ed. by D. E. Lide, CRC Press, **2007**, p. 7.
- 16 O_b is the bridging oxygen atom shared by two tungsten atoms between two different W_3O_{13} triads, O_c is the bridging atom shared by two tungsten atoms within a W_3O_{13} triad, and O_t is the terminal oxygen atom bonded to only one tungsten atom.
- 17 J. Niu, J. Zhao, D. Guo, J. Wang, *J. Mol. Struct.* **2004**, *692*, 223.
- 18 M. A. Fedotov, B. Z. Pertsikov, D. K. Danovich, *Polyhedron* **1990**, *9*, 1249.
- 19 Supporting Information is available electronically on the CSJ-Journal Web site, <http://www.csj.jp/journals/chem-lett/index.html>.
- 20 A strong and stable association would differentiate free and pro-associated polyanions in ^{31}P NMR spectroscopy.