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Oxidation Resistant Inorganic-Porphyrin Analog Polyoxometalates. 3.[1] The Synthesis and X-ray Crystallographic Characterization of a New Heteropolyoxoanion Structural Type, the Diruthenium–Oxo-Bridged "Bimetallic Inorganic-Porphyrin Analog" $KLi_{15}[O\{Ru^{IV}Cl(\alpha_2\text{-}P_2W_{17}O_{61})\}_2]\cdot 2KCl\cdot 60H_2O$

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Oxidation resistant, polyoxoanion-based, "inorganic-porphyrin analog"[2] catalysts are of considerable current interest.[1,3-7] This is especially true for those which function with the preferred oxidant,[5] O_2, or those few cases where the catalyst precursors have been unequivocally characterized,[1b,3,7] such as in the $M(OH_2)P_2W_{17}O_{61}{}^{n-}$ series[1] ($M = Mn^{3+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}$). Polyoxoanions which contain ruthenium[3d,e] accrue additional interest for two reasons: because of the activation of dioxygen by certain metalloporphyrin and other Ru complexes[8-11] and because of the rich and extensive multielectron redox chemistry displayed by ruthenium.[12-14]

We report herein the synthesis and characterization, by single-crystal X-ray crystallography, of a Ru-incorporated[15] polyoxoanion,[5,8,16] the first X-ray crystallographically characterized Ru heteropolyoxoanion complex and also the first crystallographic structure for a polyoxo*tungstate* which contains a second row, group 8 transition metal ion.[3e,17] Moreover, our results define a new polyoxoanion structural type, an oxo-bridged-dimer anion of general formula $[O\{Ru^{IV}Cl(\alpha_2\text{-}P_2W_{17}O_{61})\}_2]^{16-}$ that is structurally analogous to bimetallic metalloporphyrins containing a μ-oxo M–O–M bridge. Our results also suggest a reinvestigation of a recent report of a Ru–polyoxoanion complex that was not

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(1) (a) Part 2: Mansuy, D.; Bartoli, J.-F.; Battioni, P.; Lyon, D. K.; Finke, R. G. *J. Am. Chem. Soc.* **1991**, *113*, 7222. (b) Part 1: Lyon, D. K.; Miller, W. K.; Novet, T.; Domaille, P. J.; Evitt, E.; Johnson, D. C.; Finke, R. G. *J. Am. Chem. Soc.* **1991**, *113*, 7209.

(2) (a) Baker, L. C. W.; Figgis, J. S. *J. Am. Chem. Soc.* **1970**, *92*, 3794. (b) Baker, L. C. W. Presented at the Plenary Lecture, XV Int. Conf. on Coord. Chem., Proceedings, Moscow, 1973.

(3) (a) Katsoulis, D. E.; Pope, M. T. *J. Am. Chem. Soc.* **1984**, *106*, 2737. (b) Katsoulis, D. E.; Pope, M. T. *J. Chem. Soc., Chem. Commun.* **1986**, 1186. (c) Katsoulis, D. E.; Pope, M. T. *J. Chem. Soc., Dalton Trans.* **1989**, 1483. (d) Rong, C.; Pope, M. T. Abstracts of Papers, The 1989 International Chemical Congress of the Pacific Basin Societies, Honolulu, HI, 1989, INORG 774. (e) Rong, C.; Pope, M. T. *J. Am. Chem. Soc.* **1992**, *114*, 2932.

(4) (a) Hill, C. L.; Brown, R. B., Jr. *J. Am. Chem. Soc.* **1986**, *108*, 536. (b) *Activation and Functionalization of Alkanes*; Hill, C. L., Ed.; Wiley-Interscience: New York, 1989. (c) Faraj, M.; Hill, C. L. *J. Chem. Soc., Chem. Commun.* **1987**, 1487.

(5) Lyons, J. E.; Ellis, P. E., Jr.; Myers, H. K., Jr.; Slud, G.; Langdale, W. A. U.S. Patent 4,803,187, 1989.

(6) (a) Neumann, R.; Abu-Gnim, C. *J. Chem. Soc., Chem. Commun.* **1989**, 1324. (b) Neumann, R.; Abu-Gnim, C. *J. Am. Chem. Soc.* **1990**, *112*, 6025. (c) Neumann, R.; Levin, M. *Dioxygen Activation and Homogeneous Catalytic Oxidation*; Simándi, L. I., Ed.; Elsevier Science Publishers: Amsterdam, 1991; pp 121–127.

(7) (a) Weakley, T. J. R. *Polyhedron* **1987**, *6*, 931. (b) Jorris, T. L.; Kozik, M.; Casan-Pastor, N.; Domaille, P. J.; Finke, R. G.; Miller, W. K.; Baker, L. C. W. *J. Am. Chem. Soc.* **1987**, *109*, 7402.

(8) (a) Collman, J. P.; Barnes, C. E.; Collins, T. J.; Brothers, P. J.; Gallucci, J.; Ibers, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 7030. (b) Collman, J. P.; Barnes, C. E.; Brothers, P. J.; Collins, T. J.; Ozawa, T.; Gallucci, J. C.; Ibers, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 5151. (c) Collman, J. P.; Brauman, J. I.; Fitzgerald, J. P.; Sparapany, J. W.; Ibers, J. A. *J. Am. Chem. Soc.* **1988**, *110*, 3486.

(9) (a) Groves, J. T.; Ahn, K.-H.; Quinn, R. *J. Am. Chem. Soc.* **1988**, *110*, 4217. (b) Groves, J. T.; Quinn, R. *Inorg. Chem.* **1984**, *23*, 3844. (c) Groves, J. T.; Ahn, K.-H. *Inorg. Chem.* **1987**, *26*, 3831. (d) Groves, J. T.; Quinn, R. *J. Am. Chem. Soc.* **1985**, *107*, 5790. (e) Groves, J. T.; Quinn, R. U.S. Patent 4,822,899, 1989.

(10) (a) Masuda, H.; Taga, T.; Osaki, K.; Sugimoto, H.; Mori, M.; Ogoshi, H. *J. Am. Chem. Soc.* **1981**, *103*, 2199. (b) Masuda, H.; Taga, T.; Osaki, K.; Sugimoto, H.; Mori, M.; Ogoshi, H. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 3887.

(11) (a) Kadish, K. M.; Tagliatesta, P.; Hu, Y.; Deng, Y. J.; Mu, X. H.; Bao, L. Y. *Inorg. Chem.* **1991**, *30*, 3737. (b) Maux, P. L.; Bahri, H.; Simonneaux, G. *J. Chem. Soc., Chem. Commun.* **1991**, 1350. (c) Che, C.-M.; Leung, W.-H.; Poon, C.-K. *J. Chem. Soc., Chem. Commun.* **1987**, 173. (d) Che, C.-M.; Leung, W.-H. *J. Chem. Soc., Chem. Commun.* **1987**, 1376. (e) Che, C.-M.; Wong, K.-Y.; Poon, C.-K. *Inorg. Chem.* **1985**, *24*, 1797. (f) Che, C.-M.; Poon, C.-K. *Pure Appl. Chem.* **1988**, *60*, 495. (g) Leung, W.-H.; Che, C.-M. *J. Am. Chem. Soc.* **1989**, *111*, 8812. (h) Che, C.-M.; Tang, W.-T.; Lee, W.-O.; Wong, W.-T.; Lai, T.-F. *J. Chem. Soc., Dalton Trans.* **1989**, 2011. (i) Che, C.-M.; Tang, W.-T.; Wong, W.-T.; Lai, T.-F. *J. Am. Chem. Soc.* **1989**, *111*, 9048. (j) Che, C.-M.; Wong, K.-Y. *J. Chem. Soc., Dalton Trans.* **1989**, 2065. (k) James, B. R. *Inorg. Chim. Acta, Rev.* **1970**, 73. (l) Seyler, J. W.; Leidner, C. R. *Inorg. Chem.* **1990**, *29*, 3636. (m) Balavoine, G.; Eskenazi, C.; Meunier, F.; Rivière, H. *Tetrahedron Lett.* **1984**, *25*, 3187. (n) Khan, M. M. T.; Chatterjee, D.; Merchant, R. R.; Bhatt, A.; Kumar, S. S. *J. Mol. Catal.* **1991**, *66*, 289. (o) Khan, M. M. T.; Mirza, S. A.; Sreelatha, Ch.; Abdi, S. H. R.; Shaikh, Z. A. The Role of Oxygen in Chemistry and Biochemistry. Ando, W., Moro-oka, Y., Eds.; Proc. Int. Symp. Activation of Dioxygen and Homogen. Catal. Oxidations, Tsukuba, Jpn, July 12–16, 1987; *Stud. Org. Chem.* **1988**, *33*, 211. (p) Schröder, M.; Griffith, W. P. *J. Chem. Soc., Chem. Commun.* **1979**, 58. (q) Green, G.; Griffith, W. P.; Hollinshead, D. M.; Ley, S. V.; Schröder, M. *J. Chem. Soc., Perkins Trans. I* **1984**, 681. (r) Griffith, W. P.; White, A. D. *Proc. Indian Natl. Sci. Acad.* **1986**, *A52*, 804. (s) Gagné, R. R.; Marks, D. N. *Inorg. Chem.* **1984**, *23*, 65. (t) Goldstein, A. S.; Drago, R. S. *J. Chem. Soc., Chem. Commun.* **1991**, 21.

(12) (a) Moyer, B. A.; Meyer, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 3601. (b) Moyer, B. A.; Thompson, M. S.; Meyer, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 2310. (c) Moyer, B. A.; Meyer, T. J. *Inorg. Chem.* **1981**, *20*, 436. (d) Roecker, L.; Kutner, W.; Gilbert, J. A.; Simmons, M.; Murray, R. W.; Meyer, T. J. *Inorg. Chem.* **1985**, *24*, 3784. (e) Doppelt, P.; Meyer, T. J. *Inorg. Chem.* **1987**, *26*, 2027.

(13) (a) Che, C.-M.; Wong, K.-Y.; Anson, F. C. *J. Electroanal. Chem.* **1987**, *226*, 211. (b) Ho, C.; Che, C.-M.; Lau, T.-C. *J. Chem. Soc., Dalton Trans.* **1990**, 967.

(14) (a) Haga, M.-A.; Ano, T.-A.; Kano, K.; Yamabe, S. *Inorg. Chem.* **1991**, *30*, 3843. (b) Downar, D. A. J.; Honey, G. E.; Steel, P. J. *Inorg. Chem.* **1991**, *30*, 3733. (c) Krejčík, M.; Vlček, A. A. *Inorg. Chem.* **1992**, *31*, 2390. (d) Kahn, M. M. T.; Rao, A. P.; Samad, S. A.; Chatterjee, D.; Bhatt, S. D.; Merchant, R. R. *Proc. Indian Acad. Sci. (Chem. Sci.)* **1990**, *102*, 231. (e) Toma, H. E.; Cipriano, C. *J. Electroanal. Chem.* **1989**, *263*, 313. (f) Nagao, H.; Nishimura, H.; Kitanaka, Y.; Howell, F. S.; Mukaida, M.; Kakihana, H. *Inorg. Chem.* **1990**, *29*, 1693. (g) Nagao, H.; Shibayama, M.; Kitanaka, Y.; Howell, F. S.; Shimizu, K.; Mukaida, M.; Kakihana, H. *Inorg. Chim. Acta* **1991**, *185*, 75. (h) Chakravarty, A. R.; Chakravorty, A. *Inorg. Chem.* **1981**, *20*, 275. (i) Goswami, S.; Chakravarty, A. R.; Chakravorty, A. *Inorg. Chem.* **1982**, *21*, 2737. (j) Böttcher, W.; Brown, G. M.; Sutin, N. *Inorg. Chem.* **1979**, *18*, 1447. (k) Haga, M.-A.; Bond, A. M. *Inorg. Chem.* **1991**, *30*, 475. (l) Ram, M. S.; Jones, L. M.; Ward, H. J.; Wong, Y.-H.; Johnson, C. S.; Subramanian, P.; Hupp, J. T. *Inorg. Chem.* **1991**, *30*, 2928. (m) Nishimura, H.; Nagao, H.; Howell, F. S.; Mukaida, M.; Kakihana, H. *Chem. Lett.* **1988**, 491. (n) Lam, K. W.; Johnson, K. E.; Lee, D. G. *J. Electrochem. Soc.* **1978**, *125*, 1069. (o) Nazeeruddin, M. K.; Rotzinger, F. P.; Comte, P.; Grätzel, M. *J. Chem. Soc., Chem. Commun.* **1988**, 872. (p) Comte, P.; Nazeeruddin, M. K.; Rotzinger, F.; Frank, A. J.; Grätzel, M. *J. Mol. Cat.* **1989**, *52*, 63. (q) El-Hendawy, A. M.; El-Shahawi, M. S. *Polyhedron* **1989**, *8*, 2813. (r) Schauwers, J.; Meuris, L.; Heerman, L.; D'Olieslager, W. *Electrochim. Acta* **1981**, *26*, 1065. (s) Zhou, J.; Xi, W.; Hurst, J. K. *Inorg. Chem.* **1990**, *29*, 160.

(15) For a definition of polyoxoanion *framework-incorporated* complexes (as opposed to polyoxoanion-*supported* complexes) see footnote 1f in: Finke, R. G.; Rapko, B.; Domaille, P. J. *Organometallics* **1986**, *5*, 175.

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definitively characterized and which appears to be a mixture of $[Ru^{III}SiW_{11}O_{39}]^{5-}$ plus other, undefined compounds.[6b,16]

The synthesis of $K_{15}H[O\{Ru(OH)(\alpha_2\text{-}P_2W_{17}O_{61})\}_2]\cdot 28H_2O$, **1**,[18] and its chloride analog $KLi_{15}[O\{Ru^{IV}Cl(\alpha_2\text{-}P_2W_{17}O_{61})\}_2]\cdot 2KCl\cdot 60H_2O$, **2**, were accomplished as follows. The lacunary polyoxoanion $K_{10}[\alpha_2\text{-}P_2W_{17}O_{61}]\cdot 15H_2O$, **3**,[1b,18b] is dissolved in water with heating, and commercial "$RuCl_3\cdot xH_2O$" (which is actually a mixture of mono- and polymetallic oxides, hydroxides, and chlorides of ruthenium(III) and -(IV)[19]) is dissolved in water and added slowly with vigorous stirring. The last of the ruthenium is transferred with minimum amounts of distilled water. The solution is maintained at 90 °C with slow stirring for ~1 h, at which time the suspension is allowed to cool to ~50 °C. This black suspension is filtered through a medium porosity filter, and all black material is rinsed from the solid with a minimum amount of ice-cold water, leaving the brown product on the filter. The product is dissolved in a minimum amount of boiling water and allowed to precipitate first at room temperature and then in a refrigerator at 2 °C for 6–24 h. The resulting golden-brown solid product is filtered out and washed with ice-cold water, anhydrous ethanol, and diethyl ether. The yield ranged from 11 to 16% of **1**.[20] Anal. Calcd for the anhydrous product **1** (found after drying at 50 °C in vacuo for 6 days): K, 6.06 (6.09); H, 0.03 (0.08); Ru, 2.09 (2.07); P, 1.28 (1.38); Cl, 0.00 (<0.1); W, 64.6 (66.8); O, 20.7 (by difference, 18.4); H_2O for 29 water molecules, 5.22 (found, for a sample dried in an oven at 50 °C overnight by TGA from 25 to 400 °C, 4.99 and 5.46%). Recrystallization of **1** from LiCl solution by slow evaporation gave crystals of the Ru–Cl analog, **2**. Addition of water to the suspension and the mother liquor dissolved these crystals, after which concentrating the solution gave X-ray-quality, square rods of **2** in high yield (~95%). Anal. Calcd for **2** (found): K, 1.17 (1.14); Li, 1.09 (1.04); Ru, 2.02 (1.97); P, 1.24 (1.25); C., 1.42 (1.47); W, 62.6 (63.5); H, 1.21 (1.00); O (not in water), 19.7 (by difference, 18.7); H_2O, 10.82 (by TGA, 25–400 °C, 10.86). Complete synthetic details for **1** and **2** are given in the supplementary material.

The X-ray crystallographic structure determination was accomplished on a red-black prism of **2**. This crystal diffracted weakly but with narrow and symmetrical peak profiles. A summary of crystal data is given in Table I, and a few crucial bond lengths are provided in Table II. A complete table containing particulars of data collection and structure refinement and text providing a discussion of the structure determination are included in the supplementary material.

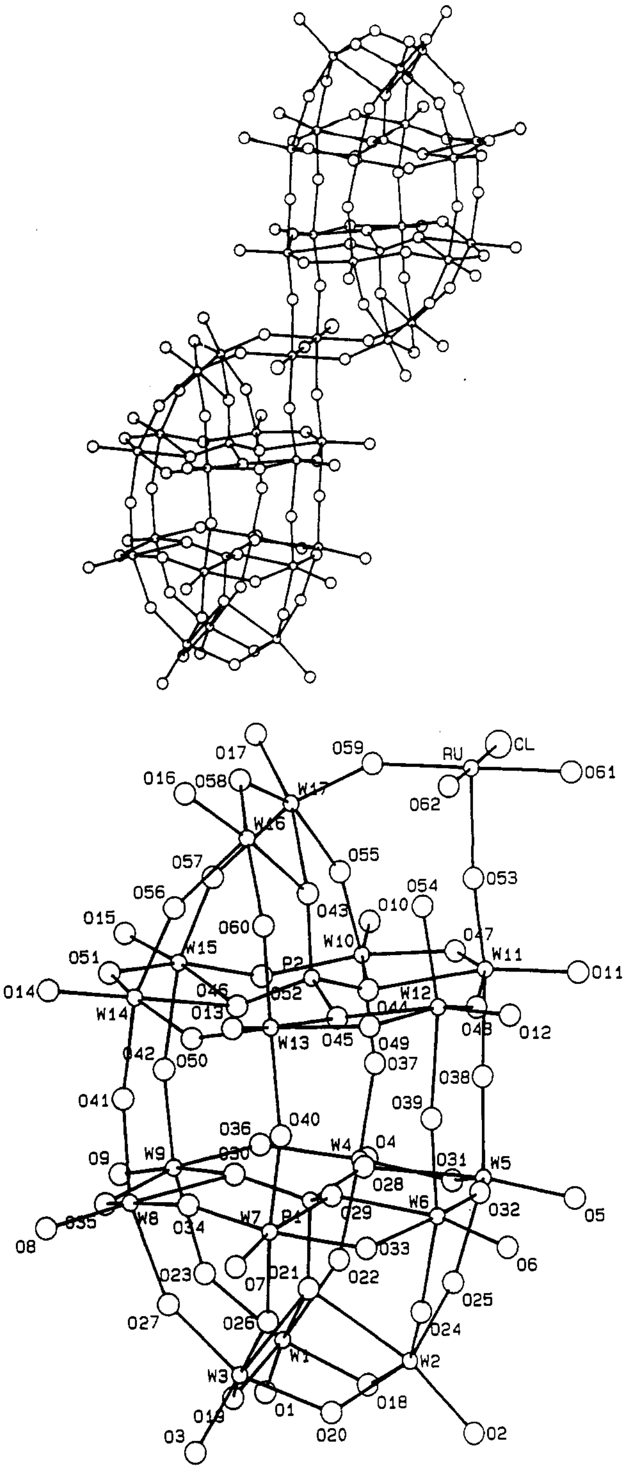

Figure 1. (a) Top: Structure of the anion of **2**. (b) Bottom: Unique asymmetric half-anion structure with atom numbering for **2**.

The structure of **2**, a "$(P_2W_{17}Ru)_2\text{–}O$" dimer with a $Ru^{IV}\text{–}O\text{–}Ru^{IV}$ linkage, is unique in the heteropolyoxoanion literature;[21] the mode of linkage of the two $\alpha\text{-}P_2W_{17}O_{61}{}^{10-}$ units is also unique. The two Ru atoms, related by a center of symmetry, are symmetrically placed *over*, rather than *in*, the lacunary site in each $\alpha\text{-}P_2W_{17}O_{61}{}^{10-}$ unit shown in Figure 1a and in the stereopair in Figure 2.

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(16) (a) There is a recent report[6b] of a ruthenium polyoxoanion complex formulated as pure "$K_5[Ru^{III}SiW_{11}O_{39}]\cdot 15H_2O$". However, our reinvestigation[16b] of the reported synthesis indicates that there is more than one compound present; the reported catalytic results apparently refer, therefore, to an unknown mixture of polyoxoanions. (b) Randall, W. J.; Finke, R. G. Unpublished results. (These results have been forwarded to Professor Neumann, who is looking into this question.)

(17) (a) Zonnevijlle, F.; Tourné, C. M.; Tourné, G. F. *Inorg. Chem.* **1982**, *21*, 2751. (b) Ortéga, F.; Pope, M. T. *Inorg. Chem.* **1984**, *23*, 3294. (c) Knoth, W. H.; Domaille, P. J.; Harlow, R. L. *Inorg. Chem.* **1986**, *25*, 1577. (d) Maksimov, G. M.; Maksimovskaya, R. I.; Matveev, K. I. *Russ. J. Inorg. Chem.* **1987**, *32*, 551.

(18) (a) Note that **1** is written at this time as $HK_{15}[O\{Ru(OH)(\alpha_2\text{-}P_2W_{17}O_{61})\}_2]$ (i.e. with a "$H^+[Ru(OH)^-]$" and not a "$[Ru(OH_2)]$" moiety) by analogy to the crystallographically characterized 16– (and thus $[KLi_{15}]^{16+}$) chloride analog **2**, $KLi_{15}[O\{Ru^{IV}Cl(\alpha_2\text{-}P_2W_{17}O_{61})\}_2]$. That is, the positions of the H^+ (aquo, hydroxo, or even a oxo formulation with 2 H^+ counterions) are not known with certainty (i.e. the difficult issue of which tautomer represents the lowest energy structure has not yet been solved). (b) Contant, R. *Inorg. Synth.* **1990**, *27*, 107.

(19) (a) Seddon, E. A.; Seddon, K. R. *The Chemistry of Ruthenium*; Elsevier: New York, 1984; pp 156–159. (b) Rard, J. A. *Chem. Rev.* **1985**, *85*, 1. (c) Bernhard, P.; Lehmann, H.; Ludi, A. *J. Chem. Soc., Chem. Commun.* **1981**, 1216. (d) Bernhard, P.; Biner, M.; Ludi, A. *Polyhedron* **1990**, *9*, 1095. (e) Harzion, Z.; Navon, G. *Inorg. Chem.* **1980**, *19*, 2236. (f) Cady, H. H.; Connick, R. E. *J. Am. Chem. Soc.* **1958**, *80*, 2646. (g) Kallen, T. W.; Earley, J. E. *Inorg. Chem.* **1971**, *10*, 1149.

(20) The low yield for this preparation is presumably a result of the nature of the ruthenium in the commercially available "$RuCl_3\cdot xH2O$", known to be a complicated and variable mixture of mono- to polymetallic $Ru^{III/IV}$ complexes.[19a-d]

(21) (a) Pope, M. T. *Heteropoly and Isopoly Oxometalates*; Springer-Verlag: Berlin, 1983. (b) Pope, M. T.; Müller, A. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 34. (c) Weakley, T. J. R. *Struct. Bonding (Berlin)* **1974**, *18*, 131.

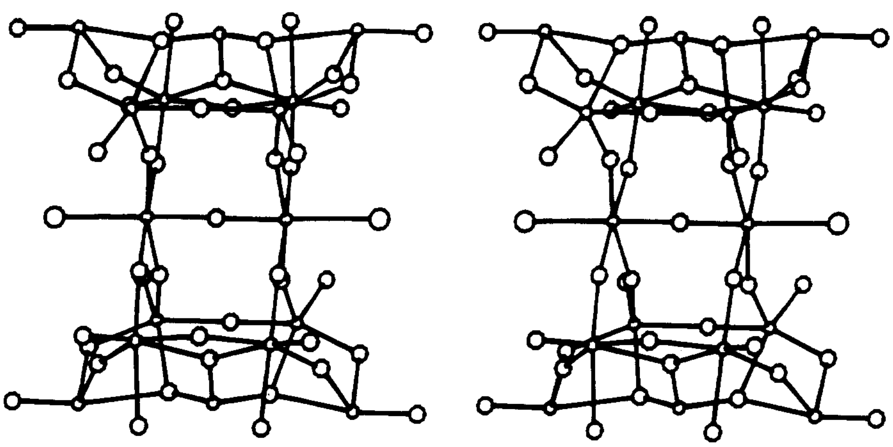

Figure 2. Stereoscopic representation of the truncated structure around the central, linear, Cl–Ru–O–Ru–Cl moiety in **2**. Note that rather than a single Ru(IV) sitting above the hole defined by four oxygens in the lacunary α_2-$P_2W_{17}O_{61}^{10-}$, the structure shows the unprecedented case of two, oxygen-bridged Ru atoms, Ru–O–Ru, sitting above the hole and connected to only two of the four oxygens which define the hole in each α_2-$P_2W_{17}O_{61}^{10-}$ polyoxoanion. Hence, two oxygens from each α_2-$P_2W_{17}O_{61}^{10-}$ define the four planar, "equatorial" oxygens of the "inorganic porphyrin-like" structure around each individual Ru(IV).

Table I. Crystallographic Data for **2**

compsn	$H_{120}Cl_4K_3Li_{15}$-	V	4000(5) Å^3
	$O_{183}P_4Ru_2W_{34}$	Z	1
fw	9989	ρ_{calc}	4.15 g cm^{-3}
space group	$P\bar{1}$	T	18 °C
a	13.220(6) Å	λ	0.710 69 Å
b	15.953(5) Å	μ	253.6 cm^{-1}
c	20.097(6) Å	rel trans coeft	0.366–1.00 (φ)
α	77.69(2)°	no. indep. obs rflns	6354 [$I \geq 3\sigma(I)$]
β	79.55(2)°	$R(F)$	0.098
γ	77.35(2)°	$R_w(F)$	0.120

Table II. Selected Bond Lengths in **2** (Å)[a]

Ru–O(53)	2.00(4)	Ru–O(62)[b]	1.773(6)
Ru–O(54)	1.94(5)	Ru–Cl	2.36(2)
Ru–O(61)	1.96(4)		

[a] Oxygen atom numbers are defined in Figure 1b. [b] Bridging, center of symmetry O.

The Ru–O–Ru unit and its rigidity effectively determines the geometry of **2**. The two α_2-$P_2W_{17}O_{61}^{10-}$ units are acting both as tetradentate chelating *and* bridging ligands to the Ru atoms, with a center of symmetry for the anion and the unit cell located at the center oxygen atom, O(62), as shown stereoscopically in Figure 2. The two sets of four oxygen atoms attached to the Ru atoms in a plane perpendicular to the Ru–O–Ru axis are eclipsed to give a local D_{4h} symmetry. The Ru–O–Ru bridge is very short and linear[8b,22] and thus presumably quite strong. The Ru–O–Ru bond lengths in **2** (1.773(6) Å) are typical of Ru^{IV}–O–Ru^{IV} (1.787(11)–1.847(13) Å[8b,22]). The Ru–Cl bond lengths (trans to the Ru–O–Ru in **2** of 2.36(2) Å) are also typical of other *trans*-O–Ru^{IV}–Cl (2.317(7)–2.505(3) Å[10b,22b,c,e,23]). Therefore, on the basis of Ru–oxygen bond lengths, valence sums,[24] bulk diamagnetism, and especially by charge balance from the analytical stoichiometry, we assign the ruthenium atoms to the +4 oxidation state. Note also that each Ru is clearly 6 and not 7 coordinate, Figure 2.[25]

The ^{31}P NMR, ^{183}W NMR, and IR spectra for $(P_2W_{17}Ru)_2$–O have also been obtained (available as supplementary material). The IR spectrum is the single easiest way to fingerprint the compound. No EPR spectrum on solid **1** at room temperature was detected over a wide range of magnetic field. This, plus the fact that no paramagnetism was observed on crystals of **2** between 10 and 310 K,[26] indicates that both **1** and **2** are diamagnetic. The ^{31}P NMR spectrum of **1** does not show the intense line broadening of the P(2) resonance as seen in the *structurally different* iron compound α_2-$P_2W_{17}O_{61}Fe(OH_2)^{7-}$;[1b] however, the position of the P(2) resonance in **1** is shifted downfield to +0.2 ppm and is about twice as broad as the P(1)[27] resonance at −13.2 ppm. (For comparison, the positions of these two resonances in the parent α_2-$P_2W_{17}O_{61}^{10-}$ are at −7.28 and −14.12 ppm, respectively.[1b]) The ^{183}W NMR spectrum for a sample of **1** in 1:1 D_2O/H_2O gave peaks (and relative integrations) at −139 (2), −161 (2), −179 (1), −183 (2), −220 (2), −222 (2), −234 (2), −236 (2), and −305 (2) ppm. Further ^{183}W 2D-NMR studies are in progress to identify the connectivities of the WO_6 octahedra in **1** and **2**.

Of significance to our plans to develop the catalytic oxidation/reduction chemistry of **1**, the dimeric structure remains intact in solution and is apparently rather stable. The solution molecular weight of **1** in 0.200 M LiCl, measured by the sedimentation–equilibrium method,[28] shows an observed MW of 8400 ± 210 amu, in excellent agreement with the calculated MW (8528 amu) for intact (dimeric) **1**. Furthermore, solutions of **1** in 0.200 M LiCl have remained unchanged for over a year by ^{31}P NMR, UV–visible (λ_{max} = 426 nm, ϵ_{426} = 1.9 × 10^4 M^{-1} cm^{-1}), and IR spectroscopies (the KBr pellet IR of solid isolated from a 0.2 M

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(22) (a) Che, C.-M.; Tang, W.-T.; Wong, W.-T.; Lai, T.-F. *J. Am. Chem. Soc.* **1989**, *111*, 9048. (b) Deloume, J.-P.; Faure, R.; Thomas-David, G. *Acta Crystallogr.* **1979**, *B35*, 558. (c) Mathieson, A. McL.; Mellor, D. P.; Stephenson, N. C. *Acta Crystallogr.* **1952**, *5*, 185. (d) Che, C.-M.; Lai, T.-F.; Wong, K.-Y. *Inorg. Chem.* **1987**, *26*, 2289. (e) Che, C.-M.; Wong, K.-Y.; Mak, T. C. W. *J. Chem. Soc., Chem. Commun.* **1985**, 988.

(23) Yukawa, Y.; Aoyagi, K.; Kurihara, M.; Shirai, K.; Shimizu, K.; Muaida, M.; Takeuchi, T.; Kakihana, H. *Chem. Lett.* **1985**, 283.

(24) Brown, I. D.; Altermatt, D. *Acta Crystallogr.* **1985**, *B41*, 244.

(25) (a) As seen in Figure 1a,b, the Ru atoms are displaced outward and away by more than one Ru^{IV} diameter (1.24–1.52 Å[25b]) from the normal eighteenth position in the Wells-Dawson α-$P_2W_{18}O_{62}^{6-}$ framework (hereafter, α-P_2W_{18}). In the α-P_2W_{18} structure the O(43) atom of one PO_4^{3-} is attached to W(18). Hence, one might suspect that Ru would be seven-coordinate in this structure. This is clearly not the case. First of all, the Ru–O(43) distance is 3.93(4) Å and the Ru′-O(43) distance is 3.91(4) Å, well beyond the van der Waals radius and thus beyond the bonding capabilities of this PO_4^{3-} pair of electrons on O(43). Second, the remaining uncoordinate pair of PO_4^{3-} electrons on O(43) are out of alignment and cannot possibly overlap with Ru. Instead, Figure 1b shows that the O(43) electron pair points essentially midway of the Ru–O–Ru vector (i.e. at the bridging oxygen O(62)) and not at an individual Ru. Thus, Ru is clearly six-coordinate in **2**. (b) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751.

(26) Randall, W. J.; Novet, T.; Johnson, D.; Finke, R. G. Unpublished results.

(27) The phosphorus labeled P(2) is the one closest to the Ru position in Figure 1.

(28) (a) Chervenka, C. H. *A Manual of Methods for the Analytical Ultracentrifuge*; Spinco Division of Beckman Instruments: Palo Alto, CA, 1969. (b) Schachman, H. K. *Methods in Enzymology*; Colowick, S. P., Kaplan, N. O., Eds.; Academic Press: New York, 1957; Vol. 4, pp 32–103. (c) Sethuraman, P. R.; Leparulo, M. A.; Pope, M. T., Zonnevijlle, F.; Brévard, C.; Lemerle, J. *J. Am. Chem. Soc.* **1981**, *103*, 7665. (d) Droege, M. W. Ph.D. Dissertation, University of Oregon, 1984, Appendix A. (e) Rhodes, D. G.; Laue, T. M. *Methods in Enzymology, Guide to Protein Purification*; Colowick, S. P., Kaplan, N. O., Eds.; Academic Press: New York, 1990; Vol. 182, pp 564–565 and 571–574.

LiCl solution of **1** proved to be the Cl^--containing **2**). It may well be, however, that the stability of **1** and especially of its Ru–O–Ru unit will mitigate *against* a rich redox chemistry for **1** (an electrochemical investigation of **1** and **2** is planned to test this issue).

Several additional questions raised by the present work will also be the focus of our future efforts. Can a more rational, higher yield synthesis to the present complex be developed? Is the Ru–O–Ru bridged structure formed under thermodynamic of kinetic control? Is **1** a catalyst for multielectron redox reactions such as H_2O oxidations or O_2 reductions or, possibly, olefin epoxidations using O_2? Interestingly, attempts to make **1** directly from commercially available $(NH_4)_4[O(RuCl_5)_2]$ *did not* give $(P_2W_{17}Ru)_2$–O but gave, instead, a low yield of yet a different compound (by ^{31}P NMR and IR). This product is being characterized currently and will be reported in due course along with studies aimed at the other questions posed above. Such results fortify Müller and Pope's recent statement that "...understanding the driving force for the formation of high-nuclearity (polyoxoanion) clusters is still a formidable challenge."[21b]

In summary, the preparation and unequivocal structural characterization of the novel polyoxoanion $[O\{Ru^{IV}Cl(\alpha_2\text{-}P_2W_{17}O_{61})\}_2]^{16-}$ has been described. This Ru-polyoxoanion provides a new type of oxidation-resistant, bimetallic Ru–O–Ru inorganic-porphyrin analog for both fundamental studies and catalysis survey experiments. It also provides a further glimpse into the rich area of Ru–polyoxometalate complexes.

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Supplementary Material Available: Text providing synthetic details, elemental analyses, and discussion of the structure determination and spectra, figures showing IR and NMR spectra, and tables listing crystallographic information, crystal structure atom coordinates, bond lengths and bond angles, and least-squares mean planes (31 pages). Ordering information is given on any current masthead page.