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FULL PAPER

Synthesis and characterization of a monoruthenium(III)-substituted Dawson polyoxotungstate derived by Br_2 oxidation of the 1 : 2 complex of ruthenium(II) and $[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$. The reactivity of *cis*-$[RuCl_2(DMSO)_4]$ as a ruthenium source

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Synthesis and characterization of the monoruthenium(III)-substituted Dawson polyoxotungstate $K_7[\alpha_2\text{-}P_2W_{17}O_{61}\text{-}Ru^{III}(H_2O)]\cdot 19H_2O$ **2**, expected to be an effective homogeneous oxidation catalyst precursor, is described. The reaction products of *cis*-$[Ru^{II}Cl_2(DMSO)_4]$ as the ruthenium source with mono-lacunary Dawson polyoxotungstate have been examined. By 5 h reaction of *cis*-$[Ru^{II}Cl_2(DMSO)_4]$ with $K_{10}[\alpha_2\text{-}P_2W_{17}O_{61}]$ in ice-cooled, HCl-acidic aqueous solution, a water-soluble 1 : 2-type diamagnetic ruthenium(II) complex, with formula $K_{18}[Ru^{II}(DMSO)_2\text{-}(P_2W_{17}O_{61})_2]\cdot 35H_2O$ **1**, was unexpectedly obtained as an analytically pure, homogeneous tan-colored solid, in which two DMSO molecules are coordinated to the ruthenium(II) atom. By Br_2 oxidation of **1**, the 1 : 1-type paramagnetic complex **2** was obtained as a black crystalline solid. Characterization of **1** and **2** has been carried out with complete elemental analysis, thermogravimetric and differential thermal analyses (TG/DTA), FT-IR, magnetic susceptibility measurements, cyclic voltammetry, UV-vis absorption and ^{31}P and ^{183}W NMR spectroscopies, as well as ^1H and ^{13}C NMR for **1**.

There is currently considerable interest in exploiting both the well defined structure of a catalyst precursor and the active site to facilitate catalysis by polyoxometalates.[1] However, it has also been stressed that it is important to discover more reliable and efficient procedures of synthesis before exploration of possible new reactivity patterns.[2] The polyoxometalates with incorporated transition metal ions have been recognized as inorganic analogs of metalloporphyrin complexes[3] and, in fact, metalloporphyrin-like catalyses such as olefin epoxidation and aliphatic and aromatic hydroxylations have been realized.[4] The 4d or 5d transition metal-ion substituted Keggin and Dawson polyoxotungstates have recently been pointed out from the viewpoints of anticipated catalysis and also the potential π-acceptor property of lacunary polyoxometalate ligands.[2] Several examples have been reported to date, such as Rh-,[2,5] Ru-,[6] Re-[7] and rare-earth metal-substituted polyoxotungstates.[8]

With regard to mono-Ru^{III}-substituted Keggin polyoxotungstates, $Cs_4[PW_{11}O_{39}Ru^{III}(H_2O)]\cdot 5H_2O$ has been synthesized by a reaction in aqueous media of $[Ru^{II}(H_2O)_6][C_7H_7SO_3]_2$ with a lacunary Keggin species $K_7[PW_{11}O_{39}]$, followed by oxidation with dioxygen,[6c] and $Cs_5[SiW_{11}O_{39}Ru^{III}(H_2O)]\cdot 7H_2O$ has very recently been obtained by a hydrothermal reaction of $Ru(acac)_3$ with $K_8[SiW_{11}O_{39}]$ under 6 MPa at 200 °C.[6g] However, the Keggin polyoxotungstate $K_5[SiW_{11}O_{39}Ru^{III}(H_2O)]$, previously prepared by reaction in an aqueous system of $RuCl_3\cdot nH_2O$ with $K_8[SiW_{11}O_{39}]$,[6a] has alternatively been proposed to be a mixture of $[SiW_{11}Ru^{III}O_{39}]^{5-}$ plus other, undefined compounds.[6d,g] Commercial $RuCl_3\cdot nH_2O$ is known to be a complicated and variable mixture of mono- or poly-meric Ru in oxidation states of three and four.[9]

On the other hand, there have been only a few examples of mono-Ru-substituted Dawson polyoxotungstates (Fig. 1a). Preliminary results on $[\alpha_2\text{-}P_2W_{17}O_{61}Ru^{III}(H_2O)]^{7-}$, contaminated with minor amounts of $[\alpha\text{-}P_2W_{18}O_{62}]^{6-}$, have been reported,[6c] which has been prepared by a reaction of mono-lacunary Dawson polyoxotungstate $K_{10}[\alpha_2\text{-}P_2W_{17}O_{61}]$ with $[Ru(H_2O)_6]\text{-}[C_7H_7SO_3]_2$, followed by oxidation with dioxygen. A related example is the first X-ray crystallographically characterized Ru^{IV}-substituted polyoxoanion, *i.e.* a μ-oxo-bridged-dimer Dawson polyoxoanion with formula $KLi_{15}[O\{Ru^{IV}Cl(\alpha_2\text{-}P_2\text{-}W_{17}O_{61})\}_2]$,[6d] which has been prepared by a reaction in aqueous media of $K_{10}[\alpha_2\text{-}P_2W_{17}O_{61}]$ with commercial $RuCl_3\cdot nH_2O$. Recently, $[Bu_4N]_7[\alpha_2\text{-}P_2W_{17}O_{61}Ru^{III}(H_2O)]$ has been reported together with the palladium(II) and iridium(IV) derivatives,[6j] but the characterization data and synthetic procedure reported are questionable.

Reported as another related ruthenium(III) complex is the sandwich-type polyoxotungstate constructed with two Keggin fragments $[WZnRu^{III}_2(OH)(H_2O)(ZnW_9O_{34})_2]^{11-}$,[10a] the catalysis of which has been reported in the hydroxylation of adamantane by dioxygen[10a–c] and alkene epoxidation by hydrogen peroxide.[10d] It has also very recently been reported that this complex is inactive for oxygenation of DTBC (3,5-di-*tert*-butylcatechol) by dioxygen at short times.[11a] From a synthetic viewpoint, we have recently made an effort to reproduce the preparation under N_2 gas of the K_{11} salt of this di-Ru^{III}-substituted polyoxotungstate, by following the literature route[10c,d] as closely as possible. However, all attempts at its isolation in a pure form have been unsuccessful and, instead, diamagnetic materials as a mixture due to incomplete substitution with the $Ru^{II}(DMSO)_n$ fragment have been obtained.[11b] Separately, we have had some problems repeating the reported synthesis of $[Bu_4N]_4[PMo_{11}O_{39}Ru^{III}(DMSO)]$ by the same research group,[6f] which has been obtained by a reaction of $[Bu_4N]_4H_3[PMo_{11}O_{39}]$ with *cis*-$[Ru^{II}Cl_2(DMSO)_4]$, *probably* in acetonitrile. In this paper,[6f] (1) an oxidation process of the

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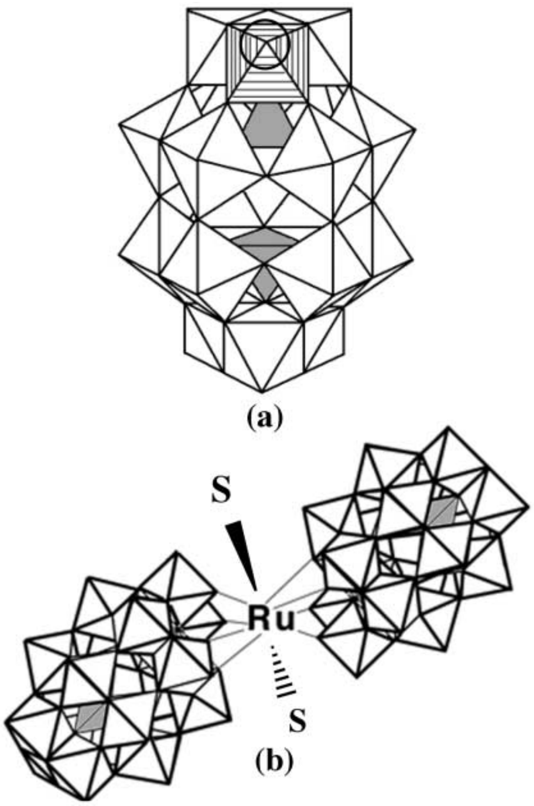

Fig. 1 Polyhedral representation of (a) the mono-M-substituted α_2-Dawson polyoxometalate $[\alpha_2\text{-}P_2W_{17}O_{61}M(H_2O)]^{2-}$ and of (b) the 1 : 2-type ruthenium(II) complex **1** with C_{2h} symmetry, giving rise to a 9-line ^{183}W NMR spectrum. In (a) the internal gray tetrahedra represent the PO_4^{3-} core, while the white octahedra represent the WO_6 fragment with a tungsten atom in the center of the octahedra and oxygen atoms at each corner. The hatched octahedron represent the octahedron of heterometal M with oxygen atoms at the vertices and the open circle represents the H_2O molecule. The two phosphorus atoms, P(1) and P(2), are defined as "close to M (north)" and "far from M (south)", respectively. In (b), S represents the S-bonding DMSO molecule.

starting Ru^{II}–DMSO bond to the Ru^{III}–DMSO bonding product is not described and (2) evidence of Ru^{III}–DMSO bond formation is not provided.

Thus, we have been interested in the reactivity of *cis*-$[Ru^{II}Cl_2(DMSO)_4]$, as a water-soluble, well defined ruthenium source,[12b] with saturated and lacunary polyoxometalates, and also in the preparation of the pure form of monoruthenium(III)-substituted Dawson polyoxotungstate. In this work, by a reaction in ice-cooled, acidic aqueous solution of $[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$ with *cis*-$[Ru^{II}Cl_2(DMSO)_4]$, the 1 : 2-type diamagnetic complex $K_{18}[Ru^{II}(DMSO)_2(P_2W_{17}O_{61})_2]\cdot 35H_2O$ **1** was unexpectedly obtained as a homogeneous tan-colored solid. In **1** the two DMSO molecules are coordinated to the Ru^{II} atom. By Br_2 oxidation of **1**, the 1 : 1-type paramagnetic ruthenium(III) complex $K_7[\alpha_2\text{-}P_2W_{17}O_{61}Ru^{III}(H_2O)]\cdot 19H_2O$ **2** was successfully derived as a black crystalline compound, which contained neither solvated nor coordinating DMSO. The complex **2** was not derived by other oxidation agents such as hydrogen peroxide and dioxygen.

Herein we report full details of a reasonable and reliable synthesis of **1** and **2**, and their unequivocal characterization.

Experimental

Materials

The following were reagent grade used as received: KCl, $RuCl_3\cdot xH_2O$, 85% H_3PO_4, $Na_2WO_4\cdot 2H_2O$, $KHCO_3$, 1.0 and 6.0 M HCl aqueous solutions (quantitative analysis grade), DMSO, ethanol, acetone, diethyl ether (all from Wako); Br_2 (Kanto); D_2O, $CDCl_3$, DMSO-d_6 (Isotec).

Instrumentation/analytical procedures

Complete elemental analyses were carried out by Mikroanalytisches Labor Pascher (Remagen, Germany). The samples were dried at room temperature under 10^{-3}–10^{-4} Torr overnight before analysis. The CHN analyses were performed using a Perkin Elmer PE2400 series II CHNS/O Analyzer (Kanagawa University). Infrared spectra were recorded on a JASCO 300 FT-IR spectrometer in KBr discs at room temperature. TG/DTA were acquired using a Rigaku TG8101D and TAS 300 data-processing system under air with a temperature ramp of 4 °C per min between 30 and 500 °C. Magnetic susceptibility measurements were carried out with a Sherwood Scientific Limited MSB-MKI magnetic balance using 17% $MnCl_2$ aqueous solution as a standard solution. UV-visible absorption spectra were recorded on a JASCO V-560 spectrophotometer.

Current–voltage curves in cyclic voltammograms were recorded on a Potentio/Galvanostat (HAB-151, Hokuto Denko Co.) and an X-Y recorder (Model F-3F, Riken Denshi Co.). Cyclic voltammograms of **1** (0.7 and 2.5 mM) and **2** (1.3 and 2.5 mM) were measured in a 0.1 M aqueous $NaHSO_4$ solution, adjusted to pH 1.0 with sulfuric acid, using a glassy-carbon working electrode, an Ag–AgCl (saturated KCl; +0.22 V *vs.* NHE) reference electrode and a platinum plate counter electrode (both sides of 1 × 1 cm; 2 cm^2) at scan rate of 10 mV s^{-1} at room temperature (25–26 °C). The aqueous solutions were bubbled with N_2 gas for 30 min before measurements, and gas-phase bubbling with N_2 gas was performed during measurements.

^1H (399.65 MHz), $^{13}C\text{-}\{^1H\}$ (100.40 MHz) and $^{31}P\text{-}\{^1H\}$ NMR (161.70 MHz) spectra in solution were recorded in 5 mm outer diameter tubes on a JEOL JNM-EX 400 FT-NMR spectrometer with a JEOL EX-400 NMR data processing system. $^{31}P\text{-}\{^1H\}$ NMR (202.47 MHz) spectra in solution were also recorded in 5 mm outer diameter tubes on a JEOL ECP 500 FT-NMR spectrometer with a JEOL ECP-500 NMR data processing system. ^1H and $^{13}C\text{-}\{^1H\}$ NMR spectra of the complexes were measured in D_2O solution with reference to internal DSS (sodium 4,4-dimethyl-4-silapentane-1-sulfonate). Chemical shifts are reported as positive for resonances downfield of DSS (δ 0). $^{31}P\text{-}\{^1H\}$ NMR spectra were measured in D_2O solution with reference to an external standard of 25% H_3PO_4 in water in a sealed capillary. Chemical shifts are reported as negative for resonances upfield of H_3PO_4 (δ 0). ^{183}W NMR (16.50 MHz) spectra were recorded in 10 mm outer diameter tubes on a JEOL JNM-EX 400 FT-NMR spectrometer equipped with a JEOL NM-40T10L low-frequency tunable probe and a JEOL EX-400 NMR data-processing system. These spectra measured in D_2O were referenced to an external standard of saturated Na_2WO_4–D_2O solution. Chemical shifts were reported as negative for resonances upfield of Na_2WO_4 (δ 0).

Synthesis

***cis*-$[Ru^{II}Cl_2(DMSO)_4]$.** Yellow powder (1.0 g) prepared according to the literature[12b] was recrystallized from DMSO solution at 90 °C. Yellow crystals were obtained in 0.65 g (65%) yield. The compound was very soluble in water, soluble in $CHCl_3$, slightly soluble in DMSO, and sparingly soluble in acetone {Found: C, 20.0; H, 4.95. Calc. for $C_8H_{24}Cl_2O_4RuS_4$ or $[RuCl_2(C_2H_6SO)_4]$: C, 19.8; H, 4.99%}. TG/DTA data: weight loss of 23.3% below 230 °C, 42.2% below 400 °C with an endothermic peak at 203 °C and exothermic peaks at 280, 329, 411 and 450 °C; decomposition began around 200 °C. FT-IR (KBr disc): 1632m, 1409m, 1310m, 1099s, 1022s, 988m, 972m, 934s, 716w, 680m, 481w, 427m cm^{-1}. UV-vis absorption (water): 298 (ε 327), 348 nm (ε 460 dm^3 mol^{-1} cm^{-1}). ^1H NMR (D_2O, 23.1 °C): δ 2.71, 3.38, 3.42, 3.47, 3.49. ^1H NMR ($CDCl_3$, 21.7 °C): δ (major peaks) 2.70, 2.74, 3.33, 3.44, 3.50, 3.53; (minor peaks) 3.42, 3.47. ^{13}C NMR (D_2O, 20.9 °C): δ (major peaks) 41.5, 47.1, 48.5, 49.5; (minor peaks) 40.7, 46.2, 47.5, 47.9, 48.1, 49.4, 49.7.

As also reported in the literature,[12b] ^{1}H NMR spectra of the compound obtained without recrystallization are very complex, the exact intensities varying from sample to sample, whereas the 6-line spectra in $CDCl_3$ (δ 2.60, 2.72, 3.32, 3.43, 3.48 and 3.50) obtained from the recrystallized material are reproducible.

$K_{10}[\alpha_2\text{-}P_2W_{17}O_{61}]\cdot 22H_2O$. The preparation was carried out according to the literature.[4b,12a] Colorless needle crystals by repeated recrystallizations from hot water were obtained in 63.3 g yield (84.6%). The compound was soluble only in hot water. FT-IR (KBr disc): 1085vs, 1052m, 1016m, 939vs, 885s, 810vs, 737vs, 601m, 527m cm^{-1}. TG/DTA data: weight loss of 7.89% below 500 °C with endothermic peaks at 39 and 88 °C; calc. 8.00% for $x = 22$ in $K_{10}[P_2W_{17}O_{61}]\cdot xH_2O$. ^{31}P NMR ($D_2O$, 18.7 °C): δ −7.00, −14.17. Literature: δ −7.28, −14.10 for the K_{10} salt and δ −7.12, −13.95 for the Li_{10} salt,[4a] and δ −7.3, −14.1 for the Li_{10} salt.[4b] ^{183}W NMR (D_2O, 23 °C): δ −113.7 (2W), −138.3 (2W), −149.2 (2W), −178.3 (2W), −180.4 (1W), −215.2 (2W), −218.3 (2W), −221.3 (2W), −239.3 (2W). Literature:[4b,13] δ −120, −143, −154, −183, −185, −220, −222, −226, −245.

$K_{18}[Ru^{II}(DMSO)_2(P_2W_{17}O_{61})_2]\cdot 35H_2O$ 1. To a stirred, ice-cooled solution of 2.00 g (0.40 mmol) $K_{10}[\alpha_2\text{-}P_2W_{17}O_{61}]\cdot 22H_2O$ dissolved in 100 mL water was added 0.20 g (0.40 mmol) of *cis*-$[RuCl_2(DMSO)_4]$, followed by adjustment of the solution to pH 2.0 with 1.0 M aqueous HCl. Stirring was continued for 5 h in an ice-cooled bath. The solution was added to 400 mL ethanol, resulting in formation of a yellow solid. After 1 h stirring and then 1 h standing in an ice-cooled bath the solution was placed in a refrigerator at 5 °C overnight. The powder formed was collected on a membrane filter (JG 0.2 μm), washed with ethanol (50 mL × 3) and diethyl ether (50 mL × 3), and dried *in vacuo* for 2 h. At this stage the yield of a tan-colored powder was 1.70 g.

Purification. All the powder was dissolved in 20 mL water and filtered through a folded filter paper (Whatman No. 2). To it 200 mL ethanol were added, resulting in formation of a tan-colored precipitate. In an ice-cooled bath, the stirring was continued for 1 h and the solution placed in a refrigerator at 5 °C overnight. The tan-colored precipitate was collected on a membrane filter (JG 0.2 μm), washed with ethanol (50 mL × 3) and diethyl ether (50 mL × 3), and dried *in vacuo*.

Tan-colored powder with formula $K_{18}[Ru^{II}(DMSO)_2(P_2W_{17}O_{61})_2]\cdot 35H_2O$, which was soluble in water, but insoluble in ethanol and ether, was obtained in 1.35 g (68.1%) yield {Found: C, 0.60; H, 0.28; K, 7.29; O, 21.7; P, 1.38; Ru, 0.74; S, 0.69; W, 67.1; total 99.78%. Calc. for $C_4H_{22}K_{18}O_{129}P_4RuS_2W_{34}$ or $K_{18}[Ru(DMSO)_2(P_2W_{17}O_{61})_2]\cdot 5H_2O$: C, 0.51; H, 0.24; K, 7.50; O, 22.0; P, 1.32; Ru, 1.08; S, 0.68; W, 66.6%}. Weight loss observed during drying overnight at room temperature under reduced pressure (10^{-3}–10^{-4} Torr) before analysis: 2.15% which corresponds to $11H_2O$. TG/DTA data: weight loss of 7.86% below 353 °C with a broad endothermic peak at 56 °C and broad exothermic peaks at 274 and 447 °C; calc. 7.92% for two DMSO and 35 water. Magnetic susceptibility (25.5 °C): 0.61 μ_B according to the formula $K_{18}[Ru^{II}(DMSO)_2(P_2W_{17}O_{61})_2]\cdot 35H_2O$ (*M* 9918.4). FT-IR (KBr disc, polyoxometalate region): 1086vs, 1053m, 1018m, 941vs, 918s, 889s, 809vs, 755vs, 601m, 528m cm^{-1}. UV-visible absorption (water): 282 nm (ε 75900 dm^3 mol^{-1} cm^{-1}). ^{31}P NMR (D_2O, 23.7 °C): δ −7.88 (1P), −13.60 (1P). ^{183}W NMR (D_2O, 20.2 °C): δ −122.9 (2W), −132.3 (2W), −170.6 (2W), −173.6 (2W), −189.2 (2W), −202.3 (2W + 1W), −204.4 (2W), −226.8 (2W). ^{1}H NMR (D_2O, 21.7 °C): δ 3.4–3.8. ^{13}C NMR (D_2O, 21.7 °C): δ 46–50.

$K_7[\alpha_2\text{-}P_2W_{17}O_{61}Ru^{III}(H_2O)]\cdot 19H_2O$ 2. A solution containing 1.0 g of **1** dissolved in 50 mL water was filtered through a folded filter paper (Whatman No. 2). In a hood, Br_2 (*ca.* 5 mL) was added to the clear yellow filtrate until the solution became brown. The solution was evaporated on a water bath at more than 80 °C to reduce its volume to *ca.* 20 mL. After cooling to room temperature, 300 mL ethanol were added. A black precipitate formed. After 1 h stirring, the precipitate was collected on a membrane filter (JG 0.2 μm), washed with ethanol (50 mL × 3), diethyl ether (50 mL × 3) and dried thoroughly by suction. The reprecipitation with ethanol was repeated. Black powder, which was soluble in water, but insoluble in ethanol and diethyl ether, was obtained in 0.29 g (29.6%) yield after reprecipitation by adding 10 mL aqueous solution to 300 mL ethanol and, separately, in 0.49 g (50.0%) yield after vapor diffusion of an internal, 20 mL aqueous solution with external, 60 mL ethanol {Found (repeat trial for CHN analysis) [repeat analysis on an independent, earlier preparation]: C, 0.13 (0.01); H, 0.13 (0.41) [0.13]; Br, 0.03 [<0.1]; K, 5.66 [5.57]; N, (0.00); O, 23.4 [22.6]; P, 1.43 [1.33]; Ru, 2.18 [2.20]; W, 68.0 [65.2]; total 101.03 [97.03]%. Calc. for $H_6K_7O_{64}P_2RuW_{17}$ or $K_7[P_2W_{17}O_{61}Ru(H_2O)]\cdot 2H_2O$: C, 0.00; H, 0.13; Br, 0.00; K, 5.96; N, 0.00; O, 22.3; P, 1.35; Ru, 2.20; W, 68.06%}. Weight loss observed during drying overnight at room temperature under reduced pressure (10^{-3}–10^{-4} Torr) before analysis: 6.22% which corresponds to $17H_2O$. TG/DTA data: weight loss of 7.47% below 500 °C with a very broad endothermic peak around 50 °C; calc. 7.34% for $x = 19$ in $K_7[P_2W_{17}O_{61}Ru^{III}(H_2O)]\cdot xH_2O$. Magnetic susceptibility (21 °C): 1.81 μ_B according to the formula $K_7[P_2W_{17}O_{61}Ru(H_2O)]\cdot 19H_2O$ (*M* 4898). FT-IR (KBr disc, polyoxometalate region): 1092vs, 1017w, 953vs, 921s, 902s, 781vs (br), 597m, 527m cm^{-1}. UV-visible absorption (water): 297 (ε 28400), 418 (ε 3281), 551 nm (ε 1898 dm^3 mol $^{-1}$ cm^{-1}). ^{31}P NMR (D_2O, 22.3 °C): δ −16.4 (<5% impurity), −17.1 ($\Delta\nu_{1/2}$ 6.9), −66.2 ($\Delta\nu_{1/2}$ 243.4 Hz). ^{183}W NMR (D_2O, 25.2 °C): δ −120.7, −131.6, −137.8, −160.4, −170.6, −178.6, −203.9.

Oxidation of **1** in water with dioxygen was examined by O_2 bubbling for 3 h at room temperature and, also, by O_2 bubbling for 3 h under refluxing conditions. These reaction mixtures were added to an excess of EtOH to give tan and green-black powders, respectively. ^{31}P NMR of the tan powder showed a two-line spectrum, being almost unchanged from that of **1**, *i.e.* δ −7.77 and −13.63, and also an enhanced signal at δ −12.75 due to $[\alpha\text{-}P_2W_{18}O_{62}]^{6-}$. On the other hand the ^{31}P NMR of the green-black powder showed many lines and no signal around δ −60. Thus, the oxidation of **1** to **2** does not take place by O_2 bubbling. Oxidation of **1** in water with 30% aqueous hydrogen peroxide was also examined at room temperature and in an ice-cooled bath. Both solutions became black and their ^{31}P NMR showed a single peak at δ −12.78, suggesting the complete decomposition of **1**.

Results and discussion

Synthetic reactions and general properties

The complex **1** with $Ru^{II} : P_2W_{17}O_{61}{}^{10-} = 1 : 2$ has unexpectedly been obtained by 5 h reaction of *cis*-$[RuCl_2(DMSO)_4]$ with $K_{10}[\alpha_2\text{-}P_2W_{17}O_{61}]$ in ice-cooled, HCl-acidic aqueous solution. By Br_2 oxidation of **1**, the complex **2** with $Ru^{III} : P_2W_{17}O_{61}{}^{10-} = 1 : 1$ has successfully been obtained.

In the present synthesis there are several key points. (1) The work-up of the synthetic reaction and the isolation of **1** require an ice-cooled temperature condition. The ^{31}P NMR spectra of both the reaction solutions and the aqueous solution containing $K_{10}[\alpha_2\text{-}P_2W_{17}O_{61}]$ and a few drops of DMSO without the ruthenium source, at elevated temperature, showed only one signal at δ −12.8 due to the $[\alpha\text{-}P_2W_{18}O_{62}]^{6-}$ polyoxoanion. (2) A recrystallized sample of *cis*-$[RuCl_2(DMSO)_4]$ should be used, because the sample obtained without recrystallization shows multiple and complicated ^{1}H NMR spectra of S-bonded DMSO (see the Experimental section). (3) For the formation of **2**, Br_2 as an oxidant was effective, while 30% aqueous hydrogen peroxide and dioxygen did not work. (4) In the synthesis of **2**, the *in situ* reaction, *i.e.* Br_2 oxidation carried out without isolation of **1**, led to the formation of compounds with lower purities in lower yields. (5) In the isolation of **2**, the vapor diffusion method on the aqueous solution after Br_2 oxidation with external ethanol resulted in higher yields of the compounds with almost the same purity as that from reprecipitation with ethanol. Compound **1** was stable in the solid state, but underwent degradation on longer standing in an aqueous solution, whereas **2** was stable both in the solid and in an aqueous solution. Compound **1** was not crystallized, while crystals of **2** were too small and not suitable for X-ray analysis.

The formation of **1** and **2** can be represented in eqns. (1) and (2), respectively.

$$cis\text{-}[RuCl_2(DMSO)_4] + 2\,K_{10}[P_2W_{17}O_{61}] \longrightarrow K_{18}[Ru^{II}(DMSO)_2(P_2W_{17}O_{61})_2]\ \mathbf{1} + 2\,KCl + 2\,DMSO \tag{1}$$

$$K_{18}[Ru^{II}(DMSO)_2(P_2W_{17}O_{61})_2]\ \mathbf{1} + \tfrac{1}{2}Br_2 + H_2O \longrightarrow K_7[P_2W_{17}O_{61}Ru^{III}(H_2O)]\ \mathbf{2} + KBr + K_{10}[P_2W_{17}O_{61}] + 2\,DMSO \tag{2}$$

Lacunary Keggin- and Dawson-type polyoxoanions, $[XM_{11}O_{39}]^{n-}$ and $[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$, respectively, are known to act usually as pentadentate ligands to guest transition metal ions, and the sixth coordination site of a particular metal ion is generally occupied by water, which can be replaced by other ligands and is sometimes lost in non-aqueous media (Fig. 1a).[3,4j] The ionic radius of Ru^{III} (0.82 Å for the 6-coordinate, low-spin geometry[14]), in comparison with that of W^{VI} (0.74 Å), suggests that Ru^{III} would fit into the lacunary site of a polyoxotungstate framework, whereas the larger Ru^{II} atom will not. Thus, formation of the 1 : 2-type complex **1** would be observed. Co^{2+}, Ni^{2+} and Cu^{2+} ions (ionic radii for the 6-coordinate, high-spin geometry are 0.89, 0.84 and 0.87 Å, respectively[14]) have afforded 1 : 1-type Dawson complexes.[4b,13] Examples of the 1 : 2 complexes of a guest transition-metal ion with two polyoxoanion ligands have been known in the addition of larger metal centers such as rare-earth metals to the lacunary Keggin and/or Dawson polyoxoanions,[8] although some exceptions have been reported in the 1 : 1 and 1 : 2 complexes of Ce^{III} with $[P_2W_{17}O_{61}]^{10-}$.[8a] Consequently, it is reasonable that the mono-Ru^{III}-substituted Dawson polyoxotungstate **2** is successfully prepared by stepwise reactions through the isolation of the 1 : 2-type Ru^{II} complex **1** (eqn. (1)) and Br_2 oxidation of **1** (eqn. (2)).

Compositional characterization

The molecular formula of **1** with 2 DMSO and 5 solvated water is established by complete elemental analysis (all elements, including oxygen, 99.78% total observed) which has been performed for a sample dried overnight at room temperature under 10^{-3}–10^{-4} Torr. The weight loss observed during drying before analysis was 2.15% which corresponds to 11 water molecules. TG/DTA measurement up to 353 °C under atmospheric conditions shows a total weight loss of 7.86% which corresponds to two DMSO and 35 water.† In the absence of any other sources of sulfur, the S analysis (calc. 0.68, found 0.69%) reflects the presence of two DMSO molecules. The ^{1}H and ^{13}C NMR spectra in D_2O suggest that the DMSO molecules coordinate to the Ru^{II} atom through S-bonding. Magnetic susceptibility measurement at 25.5 °C suggests that **1** is a diamagnetic ruthenium(II) complex (low-spin $t_{2g}{}^6$; $S = 0$) with magnetic moment of 0.61 μ_B after diamagnetic correction. The diamagnetic property of **1** is also supported by solution (^{31}P, ^{183}W, ^{1}H and ^{13}C) NMR spectra, all signals of which are found in the region usually observed for diamagnetic polyoxometalates.

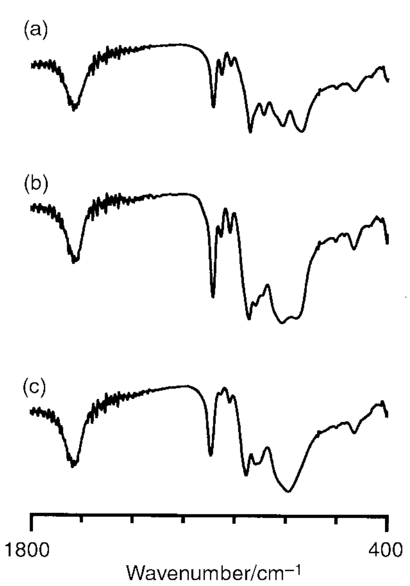

Fig. 2 The FT-IR spectra in the polyoxoanion regions, measured as KBr discs, of (a) $K_{10}[\alpha_2\text{-}P_2W_{17}O_{61}]\cdot 22H_2O$, (b) $K_{18}[Ru^{II}(DMSO)_2\text{-}(P_2W_{17}O_{61})_2]\cdot 35H_2O$ **1** and (c) $K_7[P_2W_{17}O_{61}Ru^{III}(H_2O)]\cdot 19H_2O$ **2**.

The molecular composition of **2** with two solvated water is established by complete elemental analysis (all elements, including oxygen, 101.03% total observed) which has also been performed for a sample dried overnight at room temperature under 10^{-3}–10^{-4} Torr. The ^{31}P NMR of **2** in D_2O exhibits an unavoidable minor peak at δ −16.4. The purity of **2** evaluated from the relative intensity ratio of the ^{31}P NMR was 94.8%, and consistent with that from the phosphorus analysis, *i.e.* 94.4%. Thus, the preparation of **2** is always accompanied with an impurity of *ca.* 5%. The CHN analysis, as repeat trials independently performed, also reveals the absence of DMSO molecules in **2**. Also, the bromine analysis revealed that no Br atom is contained in **2**. The weight loss of 6.22% observed during drying before analysis corresponds to 17 waters. In the TG/DTA measurements under atmospheric conditions the weight loss of 7.47% observed up to 500 °C corresponds to 19 waters, in accordance with the findings of elemental analysis and the weight loss found before analysis. Magnetic susceptibility measurement at 21 °C suggests that **2** is a paramagnetic ruthenium(III) complex (low-spin $t_{2g}{}^5$; $S = 1/2$) with magnetic moment of 1.81 μ_B after diamagnetic correction. The paramagnetic property of **2** is also supported by solution (^{31}P and ^{183}W) NMR spectra which have been influenced by the paramagnetic species.

Solid state FT-IR measurements of $K_{10}[\alpha_2\text{-}P_2W_{17}O_{61}]$ **1**, and **2** (Fig. 2a, 2b and 2c, respectively) confirm the spectral patterns characteristic of the Dawson polyoxotungstate framework.[15] The FT-IR spectrum of **1** in the polyoxometalate region is very similar to that of $K_{10}[\alpha_2\text{-}P_2W_{17}O_{61}]$, *i.e.* as found in the multiple P–O bands (1086, 1053, 1018 cm^{-1} for **1** and 1085, 1052, 1016 cm^{-1} for $K_{10}[\alpha_2\text{-}P_2W_{17}O_{61}]$), in the bands assignable to $M\text{–}O_{terminal}$ oxygens (941 cm^{-1} for **1** and 939 cm^{-1} for $K_{10}[\alpha_2\text{-}P_2W_{17}O_{61}]$) and in the bands assignable to edge-sharing M–O–M oxygens (809, 755 cm^{-1} for **1** and 810, 737 cm^{-1} for $K_{10}[\alpha_2\text{-}$

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† The inconsistency of hydrated water of compound **1** (weight loss on drying before analysis corresponding to 11 water and analytical results showing 5 water molecules) has been caused by the fact that the measurements were performed in different circumstances, *i.e.* complete elemental analysis was performed in Germany, the TG/DTA measurement in Japan. We have frequently experienced such an inconsistency. Thus, the number of hydrated waters was based on the TG/DTA measurement in Japan.

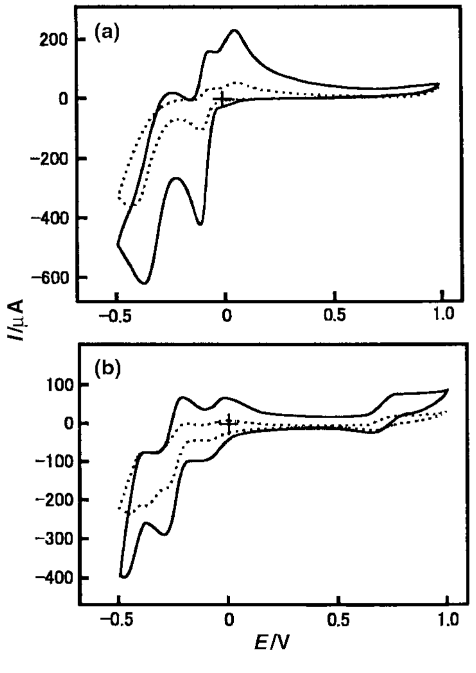

Fig. 3 Cyclic voltammograms measured in 0.1 M aqueous $NaHSO_4$ solution, adjusted to pH 1.0 with sulfuric acid, of (a) $K_{18}[Ru^{II}(DMSO)_2(P_2W_{17}O_{61})_2]\cdot 35H_2O$ **1** (full and broken lines were obtained at 2.5 and 0.7 mM concentrations, respectively) and of (b) $K_7[P_2W_{17}O_{61}Ru^{III}(H_2O)]\cdot 19H_2O$ **2** (full and broken lines were obtained at 2.5 and 1.3 mM concentrations, respectively).

$P_2W_{17}O_{61}$]). A major change was seen in the bands assignable to corner-sharing M–O–M oxygens (918, 889 cm^{-1} for **1** and 885 cm^{-1} for $K_{10}[\alpha_2\text{-}P_2W_{17}O_{61}]$). Compared with these spectra, the FT-IR spectrum of **2** showed fewer split bands: P–O (1092, 1017 cm^{-1}), $M–O_{terminal}$ (953 cm^{-1}), $M–O_{corner}–M$ (902 cm^{-1}) and $M–O_{edge}–M$ band (781 cm^{-1}). The IR spectral pattern of **2** is consistent with those of most mono-transition metal-substituted Dawson polyoxotungstates, *e.g.* the potassium salts of $[\alpha_2\text{-}P_2W_{17}O_{61}M^{n+}(H_2O)]^{(n-10)}$ ($M^{n+} = Mn^{3+}, Fe^{3+}, Co^{2+}, Ni^{2+}$ or Cu^{2+}).[4b]

Cyclic voltammetry

The cyclic voltammogram of *cis*-$[Ru^{II}Cl_2(DMSO)_4]$ showed no redox peak in the range of −0.5 to +1.0 V. The cyclic voltammogram of **1** (Fig. 3a) showed one reduction peak at −0.11 V and two oxidation peaks at −0.06 and +0.06 V, which were assignable to the $Ru^{III/II}$ couple. On the other hand, the cyclic voltammogram of **2** (Fig. 3b) showed one reduction peak at −0.11 V and an oxidation peak at −0.02 V due to the $Ru^{III/II}$ couple. A reduction peak at +0.67 V and an oxidation peak at +0.79 V were also observed. It is likely that these redox peaks are not due to reversible processes, because the potential differences are larger than 60 mV/n (n = the number of participating electrons). The cyclic voltammogram of **2** should be compared with the literature precedence;[6c] in the experiments at pH 3 for $[\alpha_2\text{-}P_2W_{17}O_{61}Ru^{III}(H_2O)]^{7-}$ carried out on a mixture with $[\alpha\text{-}P_2W_{18}O_{62}]^{6-}$, the $Ru^{III/II}$, $Ru^{IV/III}$ and $Ru^{V/IV}$ reduction potentials have been reported as −0.11, +0.62 and +0.77 V, respectively. On the other hand, a variation of the reduction potentials of $[PW_{11}O_{39}Ru^{III}(H_2O)]^{4-}$ with pH has also been reported;[6c] the $Ru^{III/II}$ and $Ru^{V/IV}$ potentials are pH independent from pH 0 to 4 and from 1 to 7, respectively, whereas the $Ru^{IV/III}$ potential varies by about 120 mV per pH unit between pH 0 and 4. At pH < 1, the two single-electron transfers of $Ru^{IV/III}$ and $Ru^{V/IV}$ coalesce to a two-electron transfer. Thus, for **2** at pH 1.0, the wave observed at +0.67 V may be attributed to the two single-electron transfers of $Ru^{V/IV}$ and $Ru^{IV/III}$ which coalesce to a two-electron transfer.

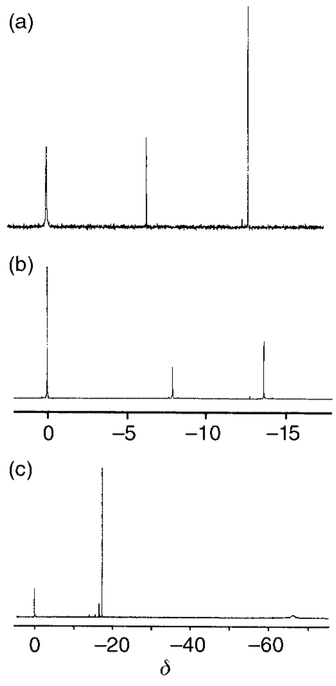

Fig. 4 Solution ^{31}P NMR spectra in D_2O of (a) $K_{10}[\alpha_2\text{-}P_2W_{17}O_{61}]\cdot 22H_2O$, (b) $K_{18}[Ru^{II}(DMSO)_2(P_2W_{17}O_{61})_2]\cdot 35H_2O$ **1** and (c) $K_7[P_2W_{17}O_{61}Ru^{III}(H_2O)]\cdot 19H_2O$ **2**.

Solution (^{31}P, ^{183}W, ^{1}H and ^{13}C) NMR spectra

The ^{31}P NMR spectrum of **1** in D_2O showed a simple two-line spectrum with resonances at δ −7.88 and −13.60 (Fig. 4b), substantially different from the resonances of $K_{10}[\alpha_2\text{-}P_2W_{17}O_{61}]$ at δ −7.00 and −14.17 (Fig. 4a), both with integrated intensities of 1 : 1 as expected for the two types of phosphorus present in the Dawson structure. The upfield resonance is known to be due to the phosphorus (P(2) atom) closer to the W_3O_6 cap (Fig. 1a), whereas the downfield resonance is assigned to the phosphorus (P(1) atom) closest to the opposite site. The two-line, impressively clean ^{31}P NMR spectrum strongly suggests the presence of a single species in solution, thereby precluding the presence of even minor, phosphorus-containing impurities in **1** and $K_{10}[\alpha_2\text{-}P_2W_{17}O_{61}]$. Further, the observed ^{31}P chemical shifts are in the usual region for diamagnetic species of various Dawson polyoxotungstates, supporting that **1** is a diamagnetic ruthenium(II) complex. The chemical shifts are compared with other data (Table 1) of the K_8 salt of $[\alpha_2\text{-}P_2W_{17}O_{61}Zn(H_2O)]^{8-}$ [4a] and the Li_8 salt,[4a,13] and $[\alpha_2\text{-}P_2W_{17}O_{61}Ru^{II}(DMSO)]^{8-}$.[6c] The minor peak at δ −12.8 due to $[\alpha\text{-}P_2W_{18}O_{62}]^{6-}$ as an impurity is sometimes observed in the ^{31}P NMR spectrum after longer standing of **1** in aqueous solution, suggesting that **1** is less stable in aqueous solution or undergoes degradation.

In contrast, the ^{31}P NMR spectrum of **2** in D_2O, consisting of a very sharp signal at δ −17.1 ($\Delta\nu_{1/2}$ 6.9 Hz) and a very broad signal at δ −66.2 ($\Delta\nu_{1/2}$ 243.4 Hz) accompanied with an unavoidable minor peak at δ −16.4 due to impurity (Fig. 4c), is clearly influenced by the paramagnetic ruthenium(III) species[13] and can be compared with other data (Table 1) of $[\alpha_2\text{-}P_2W_{17}O_{61}Ru^{III}(H_2O)]^{7-}$ measured on a mixture with $[P_2W_{18}O_{62}]^{6-}$,[6c] and with the chemical shifts of the P(2) atom observed for a series of paramagnetic M^{n+} incorporations ($M = Mn^{3+}, Fe^{3+}, Co^{2+}$ or Ni^{2+}) in $[\alpha_2\text{-}P_2W_{17}O_{61}M(H_2O)]^{n-}$,[4b] and also with the chemical shifts of the P(1) and P(2) atoms of $[\alpha_2\text{-}P_2W_{17}O_{61}M(H_2O)]^{n-}$ ($M = Co^{2+}, Mn^{3+}, Mn^{2+}$ or Ni^{2+}).[13] Compared with **1** and $K_{10}[\alpha_2\text{-}P_2W_{17}O_{61}]$, the phosphorus (P(1)) closest to the Ru^{III} atom in **2** is largely shifted upfield, whereas that (P(2)) closer to the W_3O_6 cap is less influenced.[13] The ^{31}P NMR spectrum of **2** is reproducible and usually contains an unavoidable minor peak at δ −16.4 as <5% impurity.

Table 1 ^{31}P NMR spectra in D_2O of **1** and **2**, and related Dawson polyoxotungstates

	δ ($\Delta\nu_{1/2}$/Hz)		
Complex	(P1)	(P2)	Ref.
$K_{10}[\alpha_2\text{-}P_2W_{17}O_{61}]\cdot 22H_2O$	−7.00	−14.17	This work
$K_{18}[Ru^{II}(DMSO)_2(\alpha_2\text{-}P_2W_{17}O_{61})_2]\cdot 35H_2O$ **1**	−7.88	−13.60	This work
$K_8[\alpha_2\text{-}P_2W_{17}O_{61}Zn(H_2O)]$	−8.65	−14.15	4(*a*)
$Li_8[\alpha_2\text{-}P_2W_{17}O_{61}Zn(H_2O)]$	−8.65	−14.11	4(*a*)
$Li_8[\alpha_2\text{-}P_2W_{17}O_{61}Zn(H_2O)]$	−8.0	−13.5	13
$[\alpha_2\text{-}P_2W_{17}O_{61}Ru^{II}(DMSO)]^{8-}$	−8.7 ($\Delta\nu_{1/2}$ 7.4)	−13.5 ($\Delta\nu_{1/2}$ 7.4)	6(*c*)
$K_7[\alpha_2\text{-}P_2W_{17}O_{61}Ru^{III}(H_2O)]\cdot 19H_2O$ **2**[a]	−66.2 ($\Delta\nu_{1/2}$ 243.4)	−17.1 ($\Delta\nu_{1/2}$ 6.9)	This work
$[\alpha_2\text{-}P_2W_{17}O_{61}Ru^{III}(H_2O)]^{7-}$[b]	−59.2 ($\Delta\nu_{1/2}$ 240)	−17.1 ($\Delta\nu_{1/2}$ 4.4)	6(*c*)
$[\alpha_2\text{-}P_2W_{17}O_{61}Mn^{III}(H_2O)]^{7-}$	+564 ($\Delta\nu_{1/2}$ 12300)	−12.3 ($\Delta\nu_{1/2}$ 66)	4(*b*)
$[\alpha_2\text{-}P_2W_{17}O_{61}Mn^{III}(H_2O)]^{7-}$	+575	−12.5	13
$[\alpha_2\text{-}P_2W_{17}O_{61}Mn^{II}(H_2O)]^{8-}$	+600	−13.4	13
$[\alpha_2\text{-}P_2W_{17}O_{61}Fe^{III}(H_2O)]^{7-}$	—	−11.9 ($\Delta\nu_{1/2}$ 65)	4(*b*)
$[\alpha_2\text{-}P_2W_{17}O_{61}Co^{II}(H_2O)]^{8-}$	—	−22.6	4(*b*)
$[\alpha_2\text{-}P_2W_{17}O_{61}Co^{II}(H_2O)]^{8-}$	+250	−23.7	13
$[\alpha_2\text{-}P_2W_{17}O_{61}Ni^{II}(H_2O)]^{8-}$	—	−14.0	4(*b*)
$[\alpha_2\text{-}P_2W_{17}O_{61}Ni^{II}(H_2O)]^{8-}$	+228	−14.0	13

[a] The spectrum contains an unavoidable minor peak at δ −16.4 as <5% impurity. [b] The spectrum has been measured on a mixture with $[P_2W_{18}O_{62}]^{6-}$.

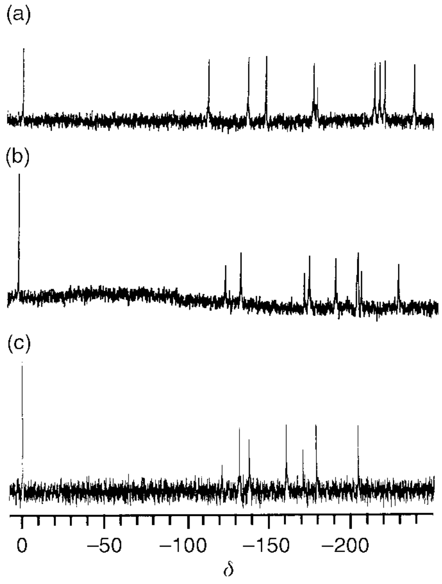

Fig. 5 Solution ^{183}W NMR spectra in D_2O of (a) $K_{10}[\alpha_2\text{-}P_2W_{17}O_{61}]\cdot 22H_2O$, (b) $K_{18}[Ru^{II}(DMSO)_2(P_2W_{17}O_{61})_2]\cdot 35H_2O$ **1** and (c) $K_7[P_2W_{17}O_{61}Ru^{III}(H_2O)]\cdot 19H_2O$ **2**.

The ^{183}W NMR spectrum of $K_{10}[\alpha_2\text{-}P_2W_{17}O_{61}]$ in D_2O (Fig. 5a) shows primarily 9 resonances at δ −113.7, −138.3, −149.2, −178.3, −180.4, −215.2, −218.3, −221.3, −239.3 with integrated intensities of 2 : 2 : 2 : 2 : 1 : 2 : 2 : 2 : 2, consistent with the C_s symmetry of a mono-lacunary Dawson structure (Fig. 1a). These results are in accord with the previous data[4b] (see the Experimental section). The ^{183}W NMR of **1** in D_2O (Fig. 5b) consists of virtually a 9-line spectrum at δ −122.9, −132.3, −170.6, −173.6, −189.2, −202.3, −204.4, −226.8 with integrated intensities of 2 : 2 : 2 : 2 : 2 : (1 + 2) : 2 : 2, in which the signal with relative intensity of 1 appears very close to the signal at δ −202.3, supporting that **1** is a 1 : 2-type complex constructed with two mono-lacunary Dawson fragments. These resonances are substantially different from those of $[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$. In the variable-temperature ^{183}W NMR spectra for $[Ln(\alpha_2\text{-}P_2W_{17}O_{61})_2]^{17-}$ (Ln = La^{III}, Yb^{III} or Lu^{III}) it has been elucidated by Francesconi and co-workers that the number of resonance lines varies depending upon the conformer formed by rotation of the two polyoxoanion lobes.[8a] As the ionic radius decreases, from La to Lu, the solution structures become less symmetrical at room temperature. In fact, for La, 9 resonances have been observed in the ratio 2 : 2 : 2 : 1 : 2 : 2 : 2 : 2 : 2, consistent with C_{2v} or C_{2h} symmetry and, for the analogs of Yb and Lu, 16 and 15 resonances, respectively. Since, in **1**, two DMSO molecules coordinate to the Ru^{II} through S-bonding as shown by ^{1}H NMR, the geometry around the Ru^{II} will be *unusually* 10-coordinate with C_{2h} symmetry. Thus, a plausible structure of **1** is shown in Fig. 1b. The ^{183}W NMR of **1** can also be compared with other data (Table 2) of $Li_8[\alpha_2\text{-}P_2W_{17}O_{61}Zn(H_2O)]$[4a,13] and $K_{15}H[O\{Ru(OH)(\alpha_2\text{-}P_2W_{17}O_{61})\}_2]$.[6d]

On the other hand, the ^{183}W NMR of the paramagnetic ruthenium(III) complex **2** in D_2O (Fig. 5c) shows an apparent 7-line spectrum at δ −120.7, −131.6, −137.8, −160.4, −170.6, −178.6, −203.9. The two resonances attributed to four WO_6 octahedra adjacent to an $Ru^{III}O_6$ octahedron are not found in the usual region, since they are the most affected by the addition of a paramagnetic Ru^{III} atom to the mono-lacunary Dawson polyoxoanion.[4b,13] These results are compared with those of potassium or lithium salts (Table 2) of a series of $[\alpha_2\text{-}P_2W_{17}O_{61}M(H_2O)]^{n-}$ with paramagnetic M^{n+} incorporation (M = Mn^{3+}, Fe^{3+}, Co^{2+} or Ni^{2+}).[4b,13]

The ^{1}H NMR spectrum of **1** in D_2O (Fig. 6b) is complex consisting of multiple lines at δ 3.4–3.8, which are indicative of S-bonded DMSO molecules.[2,12b] The control ^{1}H NMR measurements with DMSO-*h*$_6$ plus $K_{10}[P_2W_{17}O_{61}]$ in D_2O, and also with $K_{10}[P_2W_{17}O_{61}]$ in DMSO-*d*$_6$, showed only the peak due to the free DMSO at δ 2.77 and 2.50, respectively, but no peaks in the region of about 1 ppm downfield from free DMSO, suggesting that the two DMSO molecules contained in **1** coordinate to the Ru^{II} with S-bonding mode. It is likely that this DMSO coordination would also contribute to stabilization of the +II valence state of the Ru, as well as the coordination with two $[P_2W_{17}O_{61}]^{10-}$ ligands. The ^{13}C NMR spectrum of **1** in D_2O consisted of very broad signals.

Conclusion

In an attempt to prepare monoruthenium(II/III)-substituted polyoxotungstates $[\alpha_2\text{-}P_2W_{17}O_{61}Ru^{II/III}(H_2O)]^{n-}$, concerned with the reactivity of *cis*-$[RuCl_2(DMSO)_4]$ as a ruthenium source, we have unexpectedly obtained a 1 : 2 complex **1** of Ru^{II} with two lacunary Dawson polyoxotungstates $[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$. The two DMSO molecules contained in **1** coordinate to the Ru^{II} through S-bonding and contribute to stabilization of its +II valence state. The target complex **2** was successfully derived with >95% purity from **1** by Br_2 oxidation, but not by O_2 bubbling and 30% aqueous hydrogen peroxide. The reactivity of *cis*-$[RuCl_2(DMSO)_4]$ with the lacunary polyoxotungstates is much higher

Table 2 ^{183}W NMR spectra in D_2O of **1** and **2**, and related Dawson polyoxotungstates

Complex	δ	Ref.
$K_{10}[\alpha_2\text{-}P_2W_{17}O_{61}]\cdot 22H_2O$	−113.7, −138.3, −149.2, −178.3, −180.4, −215.2, −218.3, −221.3, −239.3	This work
$K_{18}[Ru^{II}(DMSO)_2(\alpha_2\text{-}P_2W_{17}O_{61})_2]\cdot 35H_2O$ **1**	−122.9, −132.3, −170.6, −173.6, −189.2, −202.3, −204.4, −226.8	This work
$Li_8[\alpha_2\text{-}P_2W_{17}O_{61}Zn(H_2O)]$	−80.05, −134.58, −176.66, −183.40, −204.70, −210.63, −211.04, −238.64	4(*a*)
$Li_8[\alpha_2\text{-}P_2W_{17}O_{61}Zn(H_2O)]$	−84.4, −138.7, −180, −186.7, −208.6, −214.8, −242.7	13
$K_{15}H[O\{Ru(OH)(\alpha_2\text{-}P_2W_{17}O_{61})\}_2]$	−139, −161, −179, −183, −220, −222, −234, −236, −305	6(*d*)
$K_7[\alpha_2\text{-}P_2W_{17}O_{61}Ru^{III}(H_2O)]\cdot 19H_2O$ **2**	−120.7, −131.6, −137.8, −160.4, −170.6, −178.6, −203.9	This work
$[\alpha_2\text{-}P_2W_{17}O_{61}Mn^{III}(H_2O)]^{7-}$	−74, −128, −238, −412, −531, −653	4(*b*)
$[\alpha_2\text{-}P_2W_{17}O_{61}Fe^{III}(H_2O)]^{7-}$	−144.6, −146.3, −151.8, −190.7, −445.9	4(*b*)
$[\alpha_2\text{-}P_2W_{17}O_{61}Co^{II}(H_2O)]^{8-}$	+533.7, +475.7, −146, −153, −200, −232, −236	13
$[\alpha_2\text{-}P_2W_{17}O_{61}Ni^{II}(H_2O)]^{8-}$	+468.3, +338.7, −142, −146, −200, −202, −230.5	13

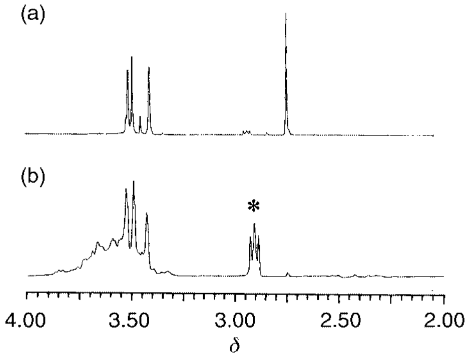

Fig. 6 ^{1}H NMR spectra in D_2O of (a) the starting *cis*-$[Ru^{II}Cl_2(DMSO)_4]$ and (b) $K_{18}[Ru^{II}(DMSO)_2(P_2W_{17}O_{61})_2]\cdot 35H_2O$ **1**. Proton signals denoted by an asterisk are from one of the methylene groups of the DSS.

than that with saturated polyoxotungstates such as sandwich polyoxotungstates under similar conditions.[11b] The present complexes are also of interest as a new type of potential, homogeneous ruthenium catalyst. This work also provides a further glimpse into the synthesis of Ru-substituted polyoxometalates using *cis*-$[Ru^{II}Cl_2(DMSO)_4]$ as the ruthenium source and the reactivity of ruthenium polyoxometalates.

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