Inorg. Chem. **2009**, *48*, 1805−1807

Inorganic Chemistry
Communication

Unprecedented Linking of Two Polyoxometalate Units with a Metal−Metal Multiple Bond

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Received December 18, 2008

The reaction of $(Bu_4N)_2[Re_2Cl_8]$ with lacunary Keggin polyoxometalate $K_7[PW_{11}O_{39}]$ in water produces a new dumbbell-shaped heteropolyoxometalate anion, $[Re_2(PW_{11}O_{39})_2]^{8-}$, whose structure contains a central Re_2 core with a quadruple bond between Re atoms (Re−Re 2.25 Å), coordinated to two polyoxometalate units. This complex represents the first example of the direct linking of two polyoxometalate units via a metal−metal multiple bond. The compounds were characterized by X-ray analysis, IR, and electrospray ionization mass spectrometry.

Polyoxometalates (POMs) are a unique class of compounds with relevance to catalysis, materials science, and medicine.[1] The most common are the Keggin-type lacunary POMs, which are known to incorporate almost all known transition and nontransition metals in the vacant site.[2] Among all of the heterometals, Re is unique in its ability to enter the POM structure in at least five oxidation states (III−VII).[3,4] The ability of Re in low oxidation states to form metal−metal (M−M) bonds is very well-known, and Re^{III} is known to have a strong tendency to form dimeric units with a Re−Re quadruple bond.[5] The work of Pope et al. on $[(Rh_2(PW_{11}O_{39})_2]^{10-}$ complexes has shown compatibility for a heterometal of being a part of the Keggin structure and participating in the M−M bonding.[6] Direct M−M bonding between two POM units can also be regarded as the simplest linker (linking the POM ions together with an organic linker with a π system has become a part of the strategy for creating new hybrid materials).[7] In this context, a new way of linking two POM units with direct participation of σ, π, and δ bonding between them offers new ways of studying the electron communication between the two POM fragments. M−M multiple-bonded complexes are catalytically active in hydrogenations, olefin metathesis, and olefin and alkyne polymerizations.[8] In this work, we report the synthesis and structure of $[Re_2(PW_{11}O_{39})_2]^{8-}$, where two Keggin-type anions, $[PW_{11}ReO_{39}]^{4-}$, are directly linked together through a short, quadruple bond between the Re atoms. This is the first example of a multiple M−M bond involvement in the chemistry of POMs.

The reaction of $[N(C_4H_9)_4]_2[Re_2Cl_8]$, which contains a Re−Re quadruple bond, with the lacunary Keggin complex $[PW_{11}O_{39}]^{7-}$ in water leads to the substitution of terminal halides with the formation of a new phosphotungstate complex, $[Re_2(PW_{11}O_{39})_2]^{8-}$, which crystallizes as $H_2(Bu_4N)_6[Re_2(PW_{11}O_{39})_2]\cdot 1.5MeCN$ (**1**) after precipitation with Bu_4N^+ and recrystallyzation from acetonitrile.[9] Crystals of similar composition, $H_2(Bu_4N)_6[Re_2(PW_{11}O_{39})_2]\cdot 1.6H_2O$ (**2**), were obtained directly from water in low yield. A competing Re dimer oxidation with complete breaking of

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10.1021/ic802373j CCC: $40.75

the Re−Re bond is observed, which leads to a mixture of simple Keggin-type complexes $[Bu_4N]_n[RePW_{11}O_{40}]$ (n = 3, 4).[3] Our attempts to increase the yield of **1** by performing the synthesis under an inert atmosphere were not successful. Probably, the POM itself acts as an oxidant in an independent reaction. Compound **1** forms brown crystals, soluble in polar organic solvents such as CH_3CN or $(CH_3)_2CO$. The most important feature of the structures of **1** and **2**[11] is the presence of a short [2.2731(9) Å in **1** and 2.269(1) Å in **2**] Re−Re bond between the two Keggin-type $\{RePW_{11}\}$ subunits. The fact that these bond distances fall within the range 2.19−2.30 Å, typically observed in complexes with a Re−Re quadruple bond, together with the eclipsed conformation of two ReO_4 units around the Re−Re axis, which is required for a $\sigma^2\pi^4\delta^2$ configuration to ensure quadruple bonding,[10] leaves no doubt that in **1** and **2** we have the Re_2^{6+} dimeric core coordinated to two lacunary Keggin phosphotungstate anions, and this leads to the overall charge of the complex at 8−.[14] In the structure of $Cs_{10}[Rh_2(PW_{11}O_{39})_2]\cdot 29H_2O$, the O_4RhRhO_4 moiety (a $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*2}$ configuration for a single Rh−Rh bond) has an eclipsed conformation.[6] The two extra protons were not directly located and are probably attached to the bridging O atoms of the POM ligands, as is often the case.[17] Each POM ligand coordinates the Re atom in a pentadentate fashion (Figure 1), so that four short and one very long Re−O bonds result. The short Re−O bonds [1.903(8)−1.931(8) Å in **1** and 1.891(10)−1.934(10) Å in **2**] are those with the four O atoms from the vacant site of $[PW_{11}O_{39}]^{7-}$, which are almost coplanar and well-suited for specific coordination requirements of the Re_2^{6+} unit. The weakly bound O atom comes from the PO_4 group [2.435(8) Å in **1** and 2.452(10) Å in **2**] and is in the position trans to the quadruple bond. The POM ligands keep their usual geometry.[15,16] The two POM ligands are related by the inversion center in the midpoint of the Re−Re bond, so that the μ_3-OReRe-μ_3-O moiety has a transoid conformation (the O−Re−Re angle is 169.2°). Another theoretically possible isomer that would result from the rotation of one {PW11} moiety by 180° is not observed. In the crystal, the $[Re_2(PW_{11}O_{39})_2]^{8-}$ dumbbells follow distorted motifs of primitive hexagonal (in **1**) and distorted face-centered-cubic (in **2**) packing, where the anions are completely isolated from one another by cations.

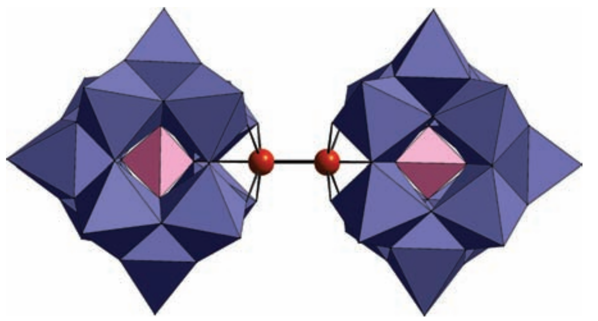

Figure 1. Polyhedral view of the $[Re_2(PW_{11}O_{39})_2]^{8-}$ anion: ball representation, Re atoms; blue, WO_6 octahedra; pink, PO_4 tetrahedra.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre and allocated the deposition numbers CCDC 707635 and 707636 for compounds **1** and **2**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax +44 1223 336033; e-mail deposit@ccdc.cam.ac.uk, or www:http://www.ccdc-.cam.ac.uk).

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(9) A total of 1.00 g (0.31 mmol) of $K_7[PW_{11}O_{39}]\cdot 14H_2O$ was dissolved in 30 mL of water while stirring and heating gently (50 °C); then 0.18 g (0.16 mmol) of $[Bu_4N]_2[Re_2Cl_8]$ was added, and the pH was adjusted to 1 with 2 M HCl. The mixture was stirred for 12 h at room temperature, during which time it became brown. Then it was heated at 80 °C for 30 min and filtered to remove a brown precipitate. The filtrate was added to an aqueous solution of 1 g (3.10 mmol) of $[N(C_4H_9)_4]Br$, the precipitate was collected by filtration and dissolved in acetonitrile, and the solution was allowed to evaporate slowly in an open vial to give brown needlelike crystals of **1**. Repeated recrystallization gave pure compound **1**. Yield: 0.12 g (11% based on $\{PW_{11}\}$). Anal. Calcd for $C_{99}H_{222.5}N_{7.5}O_{78}P_2Re_2W_{22}$: C, 16.5; H, 3.1; N, 1.5. Found: C, 16.4; H 3.1; N 1.4. P:Re:W = 1.0:1.0:11.6 (EDXS). IR (KBr disk, ν/cm^{-1}): 3433 sh, 2960 s, 2934 s, 2872 s, 1949 w, 1660 w, 1627 w, 1483 s, 1381 m, 1283 w, 1152 m, 1109 s, 1075 s (P−O), 972 s (W=O), 889 s (W-μ_2-O−W), 811 s (W−μ_3-O−W), 754 s, 593 s, 516 s, 486 s.

(10) Cotton, F. A.; Walton, R. A. *Multiple Bonds between Metal Atoms*, 2nd ed.; Clarendon Press: Oxford, U.K., 1993.

(11) The diffraction data for **1** and **2** were collected on a Bruker X8APEX CCD diffractometer with Mo Kα radiation (λ = 0.710 73 Å) using combined φ and ω scans of narrow (0.5°) frames. The structure was solved by direct methods and refined by a full-matrix least-squares method against F^2 in an anisotropic approximation using the *SHELXTL* program set.[12] Absorption corrections were applied empirically using the *SADABS* program.[13] Crystal data for **1**: $C_{99}H_{222.5}N_{7.5}O_{78}P_2Re_2W_{22}$, monoclinic, space group $P2_1/c$, a = 14.2256(4) Å, b = 31.3989(11) Å, c = 18.8250(6) Å, β = 93.8180(10)°, T = 150.0(2) K, Z = 2, V = 8389.9(5) Å^3, ρ_{calc} = 2.868 g/cm^3, $2\theta_{max}$ = 54.96°, μ = 16.548 mm^{-1}, 55 012 reflections collected within $-18 \le h \le 10$, $-40 \le k \le 40$, $-22 \le l \le 24$, 19 169 unique (R_{int} = 0.0424), 13 414 $F_0 \ge 2\sigma(F)$, 968 parameters, R1 = 0.0438, wR2 = 0.1013, GOF = 1.033, residual electron density peaks of +5.661 and −2.859 e/Å^3 (all residual peaks are on W atoms), T_{min}/T_{max} = 0.551/0.718. Crystal data for **2**: $C_{96}H_{221.2}N_6O_{79.6}P_2Re_2W_{22}$, monoclinic, space group $P2_1/c$, a = 14.1599(5) Å, b = 21.1114(7) Å, c = 28.8997(10) Å, β = 103.0020(10)°, T = 100.0(2) K, Z = 2, V = 8417.7(5) Å^3, ρ_{calc} = 2.846 g/cm^3, $2\theta_{max}$ = 55.0°, μ = 16.493 mm^{-1}, 50 703 reflections collected within $-17 \le h \le 12$, $-27 \le k \le 23$, $-23 \le l \le 37$, 18 670 unique (R_{int} = 0.0594), 11 403 $F_0 \ge 2\sigma(F)$, 932 parameters, R1 = 0.0504, wR2 = 0.1093, GOF = 1.060, residual electron density peaks of +2.856 and −2.423 e/Å^3, T_{min}/T_{max} = 0.332/0.610.

(12) *SHELXTL*, version 6.22; Bruker AXS Inc.: Madison, WI, 2003.

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(14) In one of the preparations with different amounts of Bu_4NBr, crystals of $(Bu_4N)_7(H)[Re_2(PW_{11}O_{39})_2]\cdot nH_2O$ and $(Bu_4N)_4(H)_4[Re_2(PW_{11}O_{39})_2]\cdot nH_2O$ were obtained together with **1**. The overall composition was confirmed by X-ray data, but severe disorder and the poor quality of the single crystals have so far precluded satisfactory refinement.

(15) Bond distances (Å) and angles (deg) in **1**: W−μ_4-O 2.425(8)−2.464(8), W−μ_2-O_W 1.868(9)−1.952(9), W−μ_2-O_{Re} 1.865(8)−1.918(8), W−O_{term} 1.688(8)−1.710(9), P−O_W 1.525(8)−1.537(8); W−μ_4-O−W 89.1(3)−90.4(3), W−μ_4-O−P 123.9(4)−127.6(5), Re−μ_4-O−W 88.4(3)−88.7(3), Re−μ_4-O−P 123.4(4), W−μ_2-O−W 125.3(4)−128.2(4) and 150.0(5)−151.7(5), W−μ_2-O−Re 124.9(4), 126.0(4) and 147.6(4), 148.4(5), O−Re−O 72.4(3)−91.6(4) and 160.3(3), 160.7(3), O−P−O 108.7(5)−110.2(5).

(16) Bond distances (Å) and angles (deg) in **2**: W−μ_4-O 2.405(10)−2.486(10), W−μ_2-O_W 1.864(10)−1.949(11), W−μ_2-O_{Re} 1.891(10)−1.934(10), W−O_{term} 1.678(10)−1.716(11), P−O_W 1.519(10)−1.525(10) Å; W−μ_4-O−W 88.3(3)−90.0(3), W−μ_4-O−P 125.5(6)−128.4(6), Re−μ_4-O−W 87.4(3), 88.2(3), Re−μ_4-O−P 122.1(5), W−μ_2-O−W 125.1(6)−129.1(6) and 149.9(5)−153.3(6), W−μ_2-O−Re 123.8(5), 125.1(6) and 147.9(5), 149.9(6), O−Re−O 86.0(4)−92.0(4) and 160.6(4), 161.2(4), O−P−O 108.0(6)−110.5(6)°.

(17) Pope, M. T. In *Polyoxometalates. Molecular Science*; Borras-Almenar, J. J., Coronado, E., Müller, A., Pope, M., Eds.; NATO Science Series II; Kluwer Academic Publishers: Dordrecht, The Netherlands, 2001; Vol. *98*; pp 3−31.

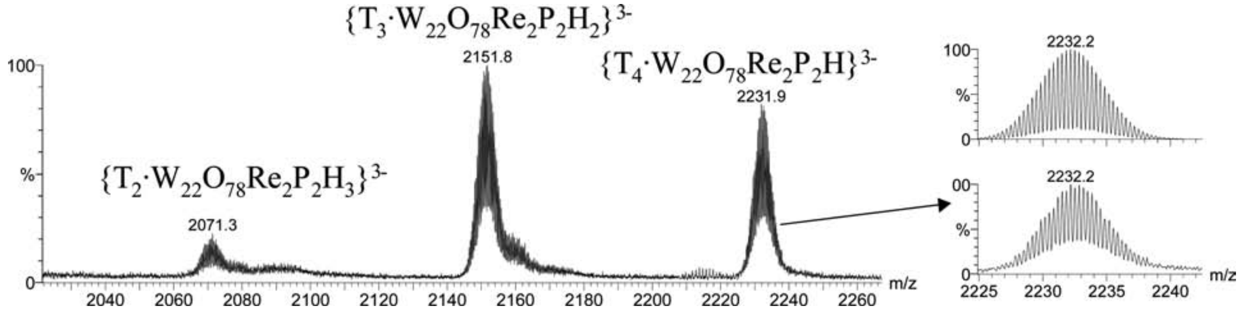

Figure 2. Negative ESI-MS spectrum of acetonitrile solutions of **1** in the range from *m/z* 2020 to 2270. T denotes tetrabutyalmmonium cations

Electrospray ionization mass spectrometry (ESI-MS) studies[18] of **1** dissolved in acetonitrile show that the dimeric moiety retained its integrity in solution. Multiply charged peaks observed in the negative ESI-MS spectrum are assigned to the series of $\{(Bu_4N)_{5-n}[Re_2(PW_{11}O_{39})_2(H_n)]\}^{3-}$ ($n = 1-3$) polyanions on the basis of *m/z* values as well as their characteristic isotopic distribution. Prominent envelopes centered at *m/z* 2071.3 ($n = 3$), 2151.8 ($n = 2$), and 2232.2 ($n = 1$) are clearly observed in the *m/z* 2020−2270 range. The negative ESI-MS spectrum of 0.05 mM acetonitrilic solutions of **1** is shown in Figure 2.

At lower *m/z* values appear minor species corresponding to the series of $\{(Bu_4N)_{4-n}[Re_2(PW_{11}O_{39})_2H_n]\}^{4-}$ ($n = 1, 2$) and $\{(Bu_4N)_{3-n}[Re_2(PW_{11}O_{39})_2H_n]\}^{5-}$ ($n = 1, 2$). The peaks from $[Re(CH_3CN)PW_{11}O_{39}]^{4-}$ are also observed, resulting from the fragmentation of $[Re_2(PW_{11}O_{39})_2]^{8-}$ by breaking of the Re−Re bond. These observations provide unambiguous proof that the intact cluster anion is present in solution and also confirm that the monoprotonated $[Re_2(PW_{11}O_{39})_2(H)]^{7-}$ and doubly protonated $[Re_2(PW_{11}O_{39}H)_2]^{6-}$ polyoxoanions represent the most favorable overall protonation of the complex. This experimental evidence corroborates the X-ray data. These observations demonstrate the potential of high-resolution ESI-MS to accurately reveal the nature of the POM cluster species in solution.[19]

In conclusion, we have succeeded in the preparation of a new dumbbell-shaped heteropolyoxometalate anion, $[Re_2(PW_{11}O_{39})_2]^{8-}$, with a central Re_2 core with a quadruple bond between Re atoms (Re−Re 2.25 Å). This complex represents the first example of the direct linking of two POM units via the M−M multiple bond. Reactivity studies, and also experiments with other multiple-bonded systems, are underway.

Acknowledgment. The work was supported by Russian Foundation for Basic Research Grants 08-03-90109 and 06-03-32831.

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(18) A Q-TOF premier mass spectrometer with an orthogonal Z-spray electrospray source (Waters, Manchester, U.K.) was used. The temperature of the source block was set to 80 °C and the desolvation temperature to 100 °C. A capillary voltage of 3.0 kV was used in the negative scan mode, and the cone voltage was set to 10 V to control the extent of fragmentation. Time-of-flight mass spectra were acquired in the V-mode operating at a resolution of ca. 10 000 (full width at half-maximum) at *m/z* 2000. Mass calibration was performed using a solution of sodium iodide in isopropyl alcohol/water (50:50) from *m/z* 100 to 2800. Acetonitrile/acetone (5:1) sample solutions were infused via a syringe pump directly connected to the ESI-MS source at a flow rate of 10 μL/min. The observed isotopic pattern of each compound perfectly matched the theoretical isotopic pattern calculated from their elemental composition using the *MassLynx* 4.1 program.

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