Tables for Supplement of the MS

Electronic Population on Tungsten, Molybdenum and Vanadium Atoms and ^{183}W, ^{95}Mo, and ^{51}V NMR in Polyoxometalates

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Table S1

Charges on tungsten calculated by EHMO and
the ^{183}W NMR chemical shifts for tungsten complexes.

	Charge q	^{183}W Chemical shift		Charge by DFT
WO_4	3.818	0		1.489
WO_3S	3.575	841		1.173
WO_2S_2	3.249	1787		0.939
WOS_3	2.9	2760		0.782
WS_4	2.529	3769		0.640
WCl_6	1.735		2181	0.648
WO_6 *	3.656		-93	1.600
WF_6	4.348		-1121	2.163
WO_5Br**	3.416		192	

* Calculated charge on W in $PW_{12}O_{40}^{3-}$

** Calculated charge on W in $PW_9O_{28}Br_6^{3-}$

Table S2

Ionization potentials, coefficients and exponents for EHMO calculations

		IP s	k	IP p	k	IP d	k	IP f	exponents					
B	5	-15.200	1.300	-8.500	1.300	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
C	6	-21.400	1.625	-11.400	1.625	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
N	7	-26.000	1.950	-13.400	1.950	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
O	8	-32.300	2.275	-14.800	2.275	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
F	9	-40.000	2.425	-18.100	2.425	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
AL	13	-12.300	1.167	-6.500	1.167	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
SI	14	-17.300	1.383	-9.200	1.383	-6.000	1.383	0.000	1.000	0.000	0.000	0.000	0.000	0.000
P	15	-18.600	1.600	-14.000	1.600	-7.000	1.600	0.000	1.000	0.000	0.000	0.000	0.000	0.000
S	16	-20.000	1.817	-13.300	1.817	-8.000	1.500	0.000	1.000	0.000	0.000	0.000	0.000	0.000
TI	22	-7.280	1.075	-4.480	0.670	-9.070	4.550	0.000	0.421	1.400	0.784	0.000	0.000	0.000
V	23	-8.530	1.200	-5.370	0.750	-10.800	4.140	0.000	0.610	1.690	0.622	0.000	0.000	0.000
CO	27	-9.210	1.700	-5.290	1.050	-13.180	5.550	0.000	0.555	1.900	0.646	0.000	0.000	0.000
ZN	30	-8.000	1.633	-4.400	1.042	-21.300	7.015	0.000	0.487	2.911	0.656	0.000	0.000	0.000
GE	32	-16.000	2.160	-9.000	1.850	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
AS	33	-16.220	2.230	-12.160	1.890	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
SE	34	-20.500	2.440	-14.400	2.070	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
BR	35	-22.070	2.588	-13.100	2.131	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
ZR	40	-9.870	1.817	-6.460	1.776	-10.180	3.835	0.000	0.622	1.505	0.578	0.000	0.000	0.000
NB	41	-9.100	1.890	-6.360	1.850	-10.100	4.280	0.000	0.640	1.640	0.552	0.000	0.000	0.000
MO	42	-8.340	1.960	-5.240	1.900	-10.500	4.540	0.000	0.590	1.900	0.590	0.000	0.000	0.000
TE	52	-20.800	2.510	-14.800	2.160	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
I	53	-18.000	2.679	-12.700	2.322	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
LA	57	-7.670	2.140	-5.010	2.080	-8.210	3.780	0.000	0.777	1.381	0.459	0.000	0.000	0.000
CE	58	-5.793	1.548	-3.908	1.361	-6.740	3.077	-10.987	0.500	1.581	0.633	0.716	2.522	0.458
W	74	-8.260	2.341	-5.170	2.309	-10.370	4.982	0.000	0.669	2.068	0.542	0.000	0.000	0.000
PB	82	-15.700	2.350	-8.000	2.060	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000

Table S3

^{183}W chemical shifts and calculated charges in derivatives based on Lindquist structure

	Anion	W_B		W_A (apical)		Ref.
		charge	δ, ppm	charge	δ, ppm	
1	$[(C_5H_5)_3U(NbW_5O_{19})_2]^{5-}$	3.707		3.666		[1]
2	$CH_3TiW_5O_{19}^{3-}$	3.733	32.3	3.744	64.5	[2]
3	$[(C_5H_5)Ti\ W_5O_{18}]^{3-}$	*3.722*	36.5	*3.749*	69.7	[2,3]
4	$H_2OZrW_5O_{18}^{2-}$	*3.760*	34.6	*3.776*	45	[4]
5	$MoW_5O_{19}^{2-}$	*3.758*	66.5	*3.737*	59.3	[5]
6	$VW_5O_{19}^{3-}$	*3.754*	76.4	*3.748*	75.9	[5]
7	$V_2W_4O_{19}^{4-}$	*3.761*	70.3	*3.753*	69.4	[5]
8	$NbW_5O_{19}^{3-}$	*3.767*	65.2	*3.754*	20.3	[5]
9	$(NbW_5O_{18})_2O^{4-}$	3.755		3.748		[5]
10	$Nb_2W_4O_{19}^{4-}$	*3.778*	86.5	*3.765*	53.2	[5]
11	$HNb_2W_4O_{19}^{3-}$		68.8		17.2	[5]

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Table S4

^{183}W NMR chemical shifts and calculated charges for halogen derivatives and dimeric forms of POM

		Type	W_a	W_b	W_c	W_d	W_e	W_f	W_g	Ref
12	$HW_{12}F_3O_{37}^{4-}$	**II**	*3.756* -90 W_9F_3	*3.697* -105.5 W_3O						[1]
13	$PW_9Br_6O_{28}^{3-}$	**II-L**	3.416 192	3.679 -123						[2]
14	$P_2W_{12}(NbO_2)_6O_{68}^{12-}$ q δ	III	3.700 *-122***	3.691 *-158*	3.660 *-204*					[3]
15	$P_2W_{21}O_{71}(H_2O)_3^{6-}$	**III-L**	3.720 -108	3.720 -109	3.634 -125	3.634 -130	3.632 -131	3.552 -152	3.639 -226	[4]
	Corrected bonds		*3.720*	*3.720*	*3.634*	*3.631*	*3.634*	*3.599*	*3.590*	
16	$As_2W_{21}O_{69}(H_2O)^{6-}$	**IV-L**	W_a	W_b	W_c	W_d	W_e	W_f	W_g	
			3.728 -141	3.729 -136	3.608 -94	3.603 -87	3.605 -103	3.665 -40	3.44 -209	[5]
	Corrected bonds		*3.664*	*3.660*	*3.669*	*3.667*	*3.666*	*3.713*	*3.493*	
17	$AsH_2W_{18}O_{60}^{7-}$	**IV-L**	H_2W_{a2}	H_2W_{b2}	AsW_{a1}	AsW_{b1}				[6,7]
	Possible assignment		3.736 *-125*	3.630 *-142.6*	3.729 *-135.8*	3.609 *-142.9*				

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Table S5

^{95}Mo NMR chemical shifts and the calculated charges

	Anion	charge		Chemical shift				Ref.
18	$Al(OH)_6Mo_6O_{18}^{-3}$	*3.777*		-18				[1]
19	$IO_6Mo_6O_{18}^{-5}$	3.801		-11				[2], [3]
20	$TeO_6Mo_6O_{18}^{-6}$	3.806		10				[4], [2]
21	$Co(OH)_6Mo_6O_{18}^{-3}$	*3.755*		69				[1][5]
22	$(Al_2Mo_{10}O_{38}H_4)^{6-}$	*3.819*	δ Mo_1	*3.754*	δ Mo_2	*3.795*	δ Mo_3	
23	$(Co_2Mo_{10}O_{38}H_4)^{6-}$	3.770	153	3.731	47	3.767	47	[6], [5]
	Δq	0.049		0.023		0.027		
24	$NiMo_9O_{32}^{6-}$	3.804	87.4	3.804	63.2			[7], [8]

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Table S6

^{51}V NMR Chemical shifts and calculated charges on vanadium.

		Type	qV_A	δ, ppm	QV_B	δ, ppm	qV_c	δ, ppm	qV_d	δ, ppm	Ref.
25	$VW_5O_{19}^{3-}$	**I-L**	*3.271*	13							[1,2]
26	$V_2W_4O_{19}^{4-}$	**I-L**	*3.284*	28							[1,2]
27	$PW_9V_3O_{40}^{6-}$	**II-L**	3.253	4							[3], [4]
28	$V_6O_{19}(CH_3)_7^-$		*3.441*	83	*3.366*	71	*3.360*	64	*3.354*	58	[5]
	^{13}C NMR		*0.406* 72.94		*0.398* 71. 27		*0.387* 70.31		*0.381* 70.08		

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Table S7

^{31}P NMR chemical shifts and difference
in the charges on phosphorous $\Delta q = q(PO_4) - q(anion)$

Anion	Δq	δ
$PMo_4O_{24}^{3-}$	0.201	5.3
$PV_{12}V_2O_{42}^{9-}$	0.197	1.0
$PV_{12}V_2O_{42}H_4^{5-}$	0.174	-1.0
$P_2Mo_{18}O_{62}^{6-}$	0.159	-2.8
$PMo_{12}O_{40}^{3-}$	0.151	-4.0
$P_2W_{18}O_{62}^{6-}$	0.145	-12.6
α $PMo_{12}O_{40}^{5-}$	0.144	-6.3
β $PMo_{12}O_{40}^{7-}$	0.141	-13.0
$PW_{12}O_{40}^{3-}$	0.137	-15.3
$PW_9O_{28}Br_6^{-3}$	0.132	-13.2

Figure captions and figures for Supplement of the MS

Electronic Population on Tungsten, Molybdenum and Vanadium Atoms and ^{183}W, ^{95}Mo, and ^{51}V NMR in Polyoxometalates

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Figure S1. Plot between the ^{183}W NMR chemical shifts and the charges on tungsten in mononuclear complexes calculated by EHMO(◆ -tetrahedral and □ -octahedral complexes) and DFT (△)methods.

Figure S2. Structures of dimeric polytungstates, polymolybdates and methylated hexavanadate.

Figure S3. HOMO for the reduced polyanions.

Figure S4. Dependence between the ^{31}P NMR chemical shifts and the difference of the charges on phosphorous, calculated for PO_4 isolated from the anion and inside of the anions.

Figure S1

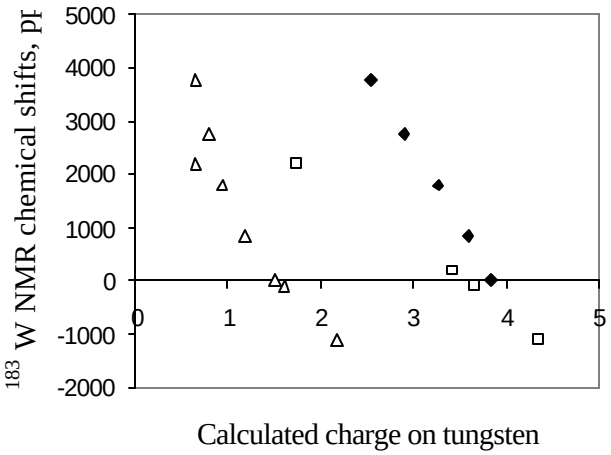
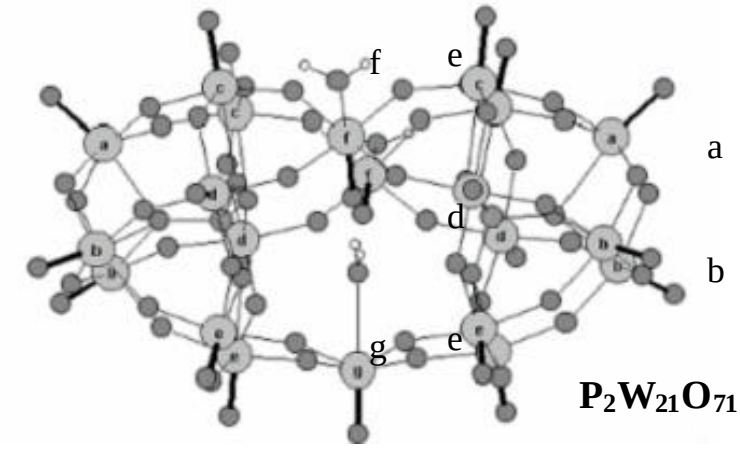
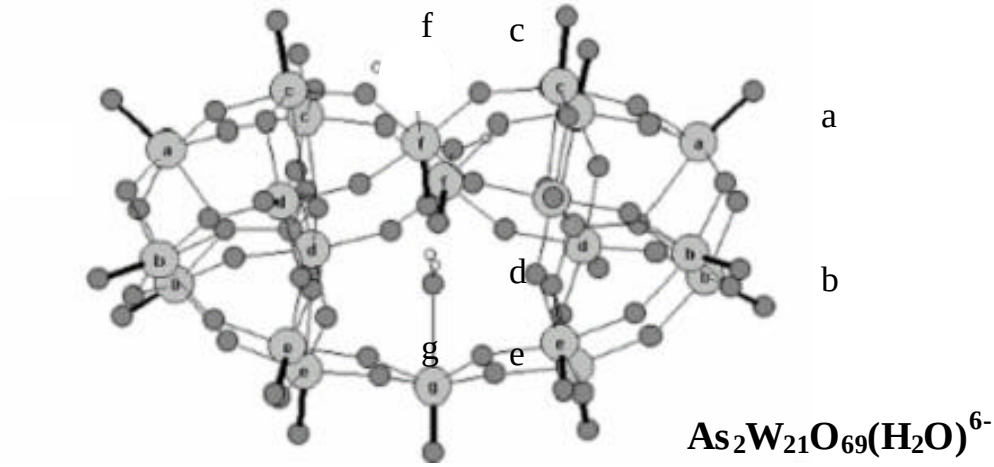


Figure S1. Plot between the ^{183}W NMR chemical shifts and the charges on tungsten in mononuclear complexes calculated by EHMO(◆ -tetrahedral and □ -octahedral complexes) and DFT (△)methods.

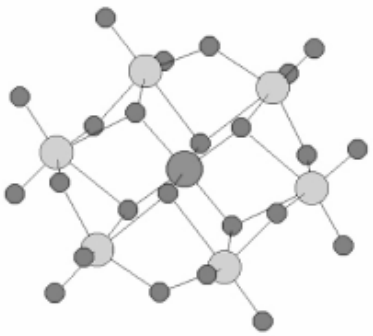
Figure S2



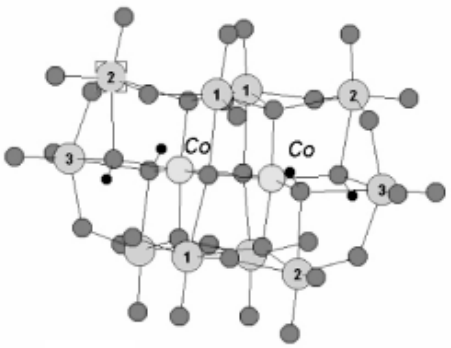
$P_2W_{21}O_{71}(H_2O)_3^{6-}$



$As_2W_{21}O_{69}(H_2O)^{6-}$

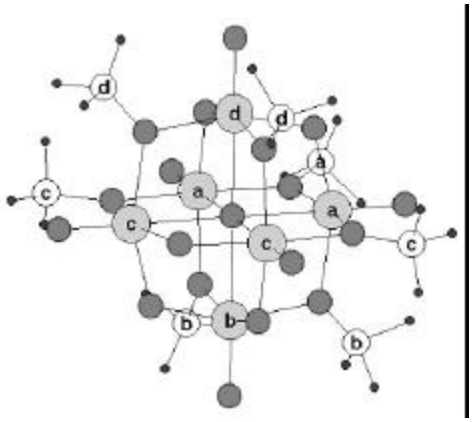


$[XMo_6O_{24}]^{n-}$



$[Co_2Mo_{10}O_{38}H_4]^{6-}$

Figure S2 continued



$[V_6O_{19}(CH_3)_7]^-$

Figure S2. Structures of dimeric polytungstates, polymolybdates and methylated hexavanadate.

Figure S3

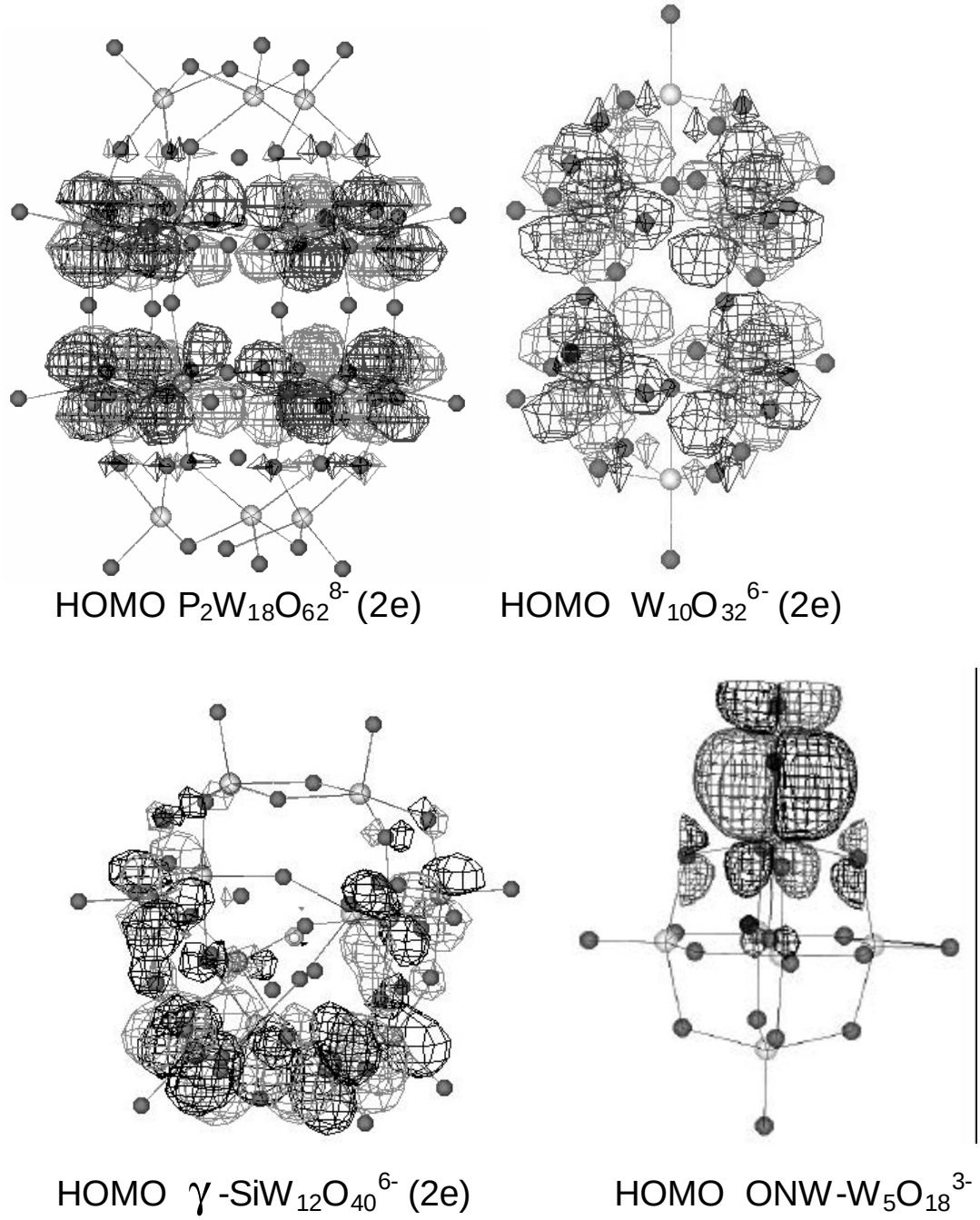


Figure S3. HOMO for the reduced polyanions.

Figure S4

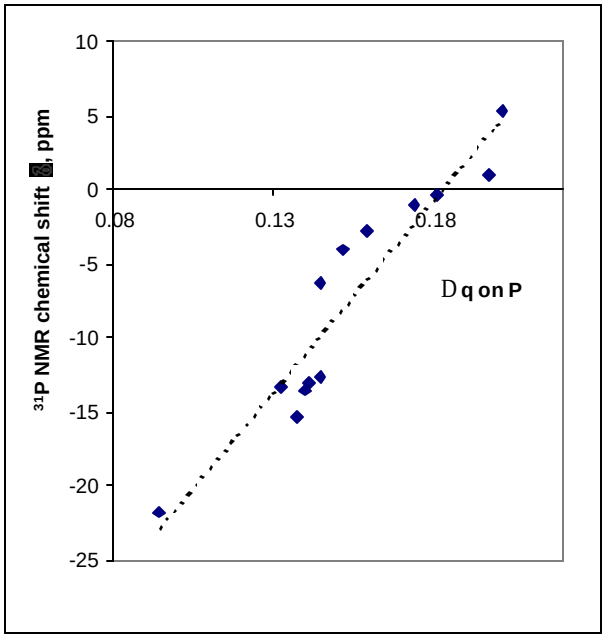


Figure S4. Dependence between the ^{31}P NMR chemical shifts and the difference of the charges on phosphorous, calculated for PO_4 isolated from the anion and inside of the anions.