Supporting Information for

Contrasting Ion-association Behaviour of Ta and Nb Polyoxometalates

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Experimental Section.

Syntheses of $K_3[Ta(O_2)_4]$, $Cs_3[Ta(O_2)_4]$, $K_8[Ta_6O_{19}] \cdot 16H_2O$ and $Cs_8[Ta_6O_{19}] \cdot 16H_2O$ have been previously reported and are summarized below.¹

K₃[**Ta**(**O**₂)₄]. Aqueous H₂O₂ (30% v/v, 40 mL) was vigorously stirred in a 600 mL beaker placed in an ice bath. TaCl₅ (4.6 g, 12.8 mmol) was added to the cold solution (*ca.* 8 °C) and the resulting thin suspension was allowed to cool back down to *ca.* 8 °C under moderate stirring. 4M aqueous KOH (35 mL) was subsequently added in small volumes and in several steps, *i.e.* the addition of base was interrupted when the temperature of the mixture was close to 20 °C and resumed once the mixture had cooled back down to *ca.* 8 °C. A white precipitate formed and then redissolved fully during this base addition step. K₃[Ta(O₂)₄] precipitated upon the addition of methanol (100 mL) to the cold (*ca.* 8 °C) clear solution. This product was finally isolated by vacuum filtration, washed with a further volume of methanol (20 mL) and dried in air. Yield = 5.4 g (99 %, Ta).

K₈[Ta₆O₁₉]·16H₂O. KOH (9.6 g, 171 mmol), K₃VO₄ (0.14 g, 0.60 mmol) and K₃[Ta(O₂)₄] (4.0 g, 9.4 mmol) were added to 25 mL of water. The resulting mixture was refluxed until the complete dissolution of the suspended materials was observed. This solution was filtrated with a 0.45 μ m nylon mesh and finally left to slowly evaporate at room temperature. After several days, colorless block crystals formed which were isolated by vacuum filtration, washed with the minimum amount of methanol and dried in air. Yield = 2.5 g (80 %, Ta).

 $Cs_3[Ta(O_2)_4]$. The procedure is the same as for the K⁺ analogue, save for the addition of 4M aqueous CsOH (32 mL) instead of the aqueous KOH. Yield = 9.0 g (99 %, Ta).

 $Cs_8[Ta_6O_{19}] \cdot 16H_2O$. The procedure is the same as for the K⁺ analogue, save for the addition of CsOH (26 g, 173 mmol) and $Cs_3[Ta(O_2)_4]$ (5.5 g, 7.8 mmol) instead of aqueous KOH and $Cs_3[Ta(O_2)_4]$ respectively. Yield = 3.0 g (85 %, Ta).

Solutions were prepared in 1M AOH (A= K, Rb, or Cs) or 1M TMAOH to the concentrations summarized in Table SI1. Solutions were contained in 2.0 mm diameter quartz capillary tubes for SAXS measurements. Small-angle X-ray scattering data were collected at beamline 12-BM-B at the Advanced Photon Source at Argonne National Laboratory with an incident photon energy of 22.0 keV. The 2D scattering profiles were collected at ambient temperature with a MAR-CCD-165 detector, which has a circular 156mm diameter active area and 2048 x 2048 pixel resolution. The sample to detector distance was adjusted to provide a detecting range for momentum transfer of $0.03 \le Q \le 1.0$ Å⁻¹. The scattering vector Q was calibrated using a silver behenate standard.² The 2D images were radially averaged to produce I(Q) vs. Q plots, where I(Q) is scattering intensity and $Q = (4\pi/\lambda)\sin(\theta/2)$ (θ is scattering angle, λ is wavelength of X-rays).



Figure SI1. Scattering intensity as a function of concentration of K₈[Ta₆O₁₉], Cs₈[Ta₆O₁₉], and Rb₈[Ta₆O₁₉] in its alkali hydroxide (KOH, RbOH, CsOH; left) and TMAOH (right).



Figure SI2a. Log(I(Q)) vs. log(Q) plots with modeled fits from SAXS data of a series of concentrations of K₈[Ta₆O₁₉] in KOH.



gure SI2b. Log(I(Q)) vs. log(Q) plots with modeled fits from SAXS data of a series o concentrations of Rb₈[Ta₆O₁₉] in RbOH.



Figure SI2c. Log(I(Q)) vs. log(Q) plots with modeled fits from SAXS data of a series of concentrations of $Cs_8[Ta_6O_{19}]$ in CsOH.



Figure SI3a. Log(I(Q)) vs log(Q) plots with modeled fits from SAXS data of a series of concentrations of K₈[Ta₆O₁₉] in TMAOH.



Figure SI3b. Log(I(Q)) vs log(Q) plots with modeled fits from SAXS data of a series of concentrations of Rb₈[Ta₆O₁₉] in TMAOH.



Figure SI3c. Log(I(Q)) vs log(Q) plots with modeled fits from SAXS data of a series of concentrations of Cs₈[Ta₆O₁₉] in TMAOH.

Table SI1. Chi squared(sum of squared standardized residuals) results obtained from the fitting of the I(Q) vs. Q with solid sphere (s), spherical shell (ss), and Moore (m) methods.

	K ₈	Ta ₆ (KO	H)	Cs ₈	Ta ₆ (CsC	DH)	Rb ₈ Ta ₆ (RbOH)			
	S SS		т	S	SS	т	S	SS	т	
0.5mM	15.197	2.6395	3.3647	75.091	72.904	72.753	3.7976	3.3619	3.6372	

2.5mM	177.63	86.038	123.88	140.87	78.574	79.055	22.252	4.0815	4.2526
5mM	228.98	23.167	9.6922	344.01	75.096	77.377	66.56	4.1758	4.5852
15mM	1196.4	35.286	40.726	1578.7	133.85	136.42	369.64	6.2869	7.4324
50mM	2320.6	406.8	536.21				410.65	30.382	18.44

	K ₈ T	a ₆ (TMA	OH)	Cs ₈ T	a ₆ (TMA	OH)	Rb ₈ Ta ₆ (TMAOH)			
	S	s ss m		S	SS	т	S	SS	т	
0.5mM	7.3591	4.6774	4.8719	69.819	69.96	69.974	6.2884	6.0551	5.5446	
2.5mM	71.753	72.081	64.613	52.331	31.997	30.478	161.95	160.75	151.91	
5mM	92.699	76.928	68.19	197.08	29.765	30.899	92.454	90.101	89.522	
15mM	1006.7	1011.3	989.91	991.8	226.82	24.029	727.21	673.3	670.49	
50mM				3398.3	2473.7	278.78	3882.4	3906.4	3561	



Figure SI4a. Guinier Analysis of I(Q) vs. Q^2 SAXS data of a series of concentrations of $Cs_8[Ta_6O_{19}]$ in TMAOH.



Figure SI4b. Guinier Analysis of I(Q) vs. Q^2 SAXS data of a series of concentrations of Rb₈[Ta₆O₁₉] in TMAOH.



Figure SI4c. Guinier Analysis of I(Q) vs. Q^2 SAXS data of a series of concentrations of K₈[Ta₆O₁₉] in TMAOH.



Figure SI5a. Guinier Analysis of I(Q) vs. Q^2 SAXS data of a series of concentrations of Cs₈[Ta₆O₁₉] in CsOH.

Figure SI5b. Guinier Analysis of I(Q) vs. Q^2 SAXS data of a series of concentrations of K₈[Ta₆O₁₉] in KOH.

Figure SI5b. Guinier Analysis of I(Q) vs. Q^2 SAXS data of a series of concentrations of Rb₈[Ta₆O₁₉] in RbOH.

Table SI2. Metrical results (Å) obtained from Guinier analysis of the $\ln(I(Q))$ vs. Q^2 data, in terms of the shape-independent radius of gyration, R_g , and from the fitting of the I(Q) vs. Q data with spherical and spherical shell form factors, which provide the sphere radii, R_S and R_{SS} , which for the latter is the sum of the spherical core radius of $[Ta_6O_{19}]^{8-}$ and the thickness of the spherical shell. The estimated standard deviations on all R obtained from the Guinier and sphere fits is ± 0.1 Å.

	1 M (H ₃ C) ₄ NOH								1 M AOH (A = K, Rb, Cs)							
[mM]		K Rb		Cs			K			Rb			Cs			
	$R_{\rm g}$	$R_{\rm S}$	$R_{\rm g}$	$R_{\rm S}$	$R_{\rm g}$	$R_{\rm S}$	$R_{\rm SS}{}^{\rm b}$	R _g	$(R_{\rm S})$	$R_{\rm SS}^{\rm c}$	$R_{\rm g}$	$(R_{\rm S})$	$R_{\rm SS}^{\rm c}$	$R_{ m g}$	$(R_{\rm S})$	$R_{\rm SS}^{\rm c}$
0.5	2.4	3.7	2.4	3.8	2.8	3.7	6.3	3.5	(4.2)	14.0 ^d	3.2	(4.5)	8.5	3.7	(4.7)	9.2
2.5	2.8	3.7	2.7	3.9	3.0	4.2	7.0	3.2	(4.2)	9.4	3.7	(4.5)	9.3	3.8	(4.8)	10.6
5.0	2.8	3.7	2.8	3.9	3.3	4.3	9.4 ^d	3.2	(4.2)	9.6	3.4	(4.5)	9.3	3.8	(4.8)	11.2
15.15	3.0	3.7	3.0	4.0	3.4	4.4	7.1	3.2	(4.0)	10.2	3.5	(4.5)	9.1	3.8	(4.8)	10.7
50.0		na ^a	3.1	4.1	3.3	4.4	6.5	3.1	(3.9)	12.5 ^d	3.3	(4.3)	7.6 ^d		naª	
AVG.	2.7(3) 3.7(0)	2.8(4)	3.9(2)	3.2(2)	4.2(5)	6.7(4)	3.2(3)		9.7(5)	3.4(3)		9.1(6)	3.8(1)		10.4(8)

^a na, not available: exceeds limit of solubility, turbid solution. ^b Goodness-of-fits in terms of reduced chi-squared values for R_{SS} model are equivalent to (0.5 mM solution) or 1.4—6.6 × better than for R_S model; therefore we present radii (R_S and R_{SS}) from both fitting models. ^c Goodness-of-fits in terms of reduced chi-squared values for R_{SS} model are 2—58 × better than for R_S model; therefore the (R_S) values are provided (parenthetically) for comparisons with the 1 M TMAOH solutions only, and are not truly descriptive of the particle morphology. ^dthese outliers we attribute to poor solution quality due to decomposition.

			(H ₃ C)	4NOH			AOH (A = K, Rb, Cs)							
[mM]	K		Rb		Cs			K		Rb		(Cs	
	<i>R</i> _g Linear Extent		R _g Linear Extent		$R_{\rm g}$ Linear Extent			$R_{\rm g}$ Linear Extent		$R_{\rm g}$ Linear Extent		$R_{\rm g}$ Linear Extent		
0.5	2.9898	8.7	3.0252	8.5	2.9667	8.5	4.	.8152	16	3.7903	13.5	4.2876	15	
2.5	2.9464	9	3.1094	8.5	3.3925	9	3.	.7958	13	4.0655	13.5	4.3602	15	
5.0	2.9272	9	3.0795	9	3.4171	10	3.	.6805	14.5	4.0488	13.5	4.5222	15	
15.15	2.9976	8.7	3.2415	9	3.5700	10.5	3.	.5928	14	3.9396	13	4.4981	15.2	
50.0	Na	1	3.3154	9.5	3.6793	10	3.	.1456	13.3	3.6023	13		na	

Table SI3. Radius of gyration (R_g) and linear extent of Pair Distance Distribution Function (PDDF) using the method of Moore in Irena.^[2]

REFERENCES

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