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Supporting Information

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Alkali-Metal-Controlled Self-Assembly of Crown-Shaped Ring Complexes of Lanthanide/$[\alpha\text{-}AsW_9O_{33}]^{9-}$: $[K\subset\{Eu(H_2O)_2(\alpha\text{-}AsW_9O_{33})\}_6]^{35-}$ and $Cs\subset\{Eu(H_2O)_2(\alpha\text{-}AsW_9O_{33})\}_4]^{23-}$

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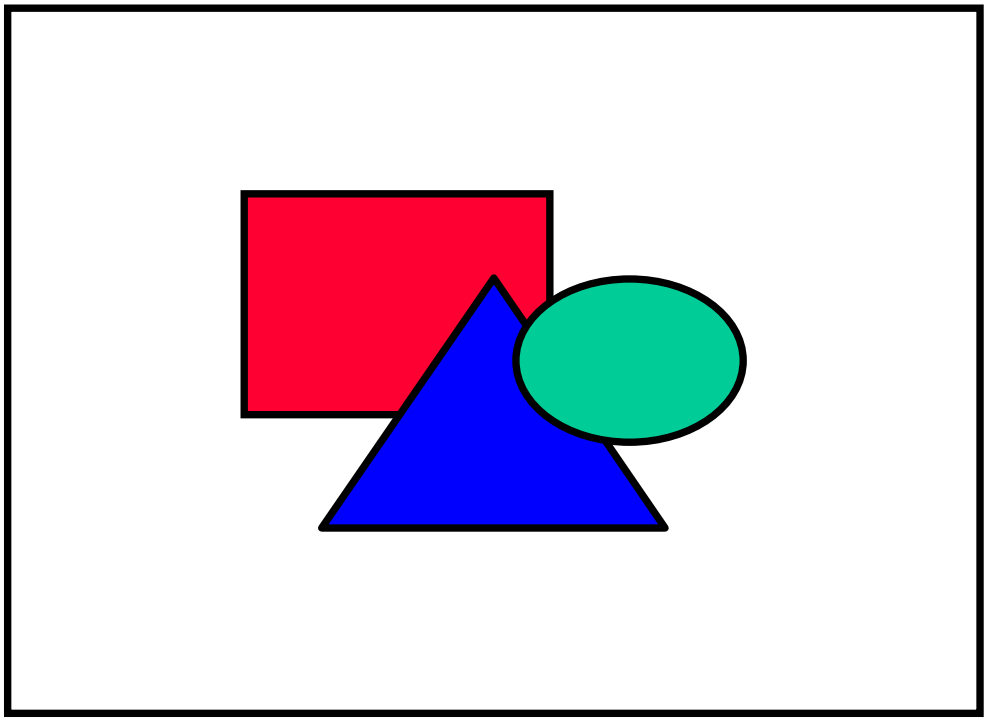

Synthesis **2**:

A solution of $Na_2WO_4.2H_2O$ (19.8g, 60mmol) and $NaAsO_2$ (0.87g, 6.7mmol) in water (60mL) was heated at approximately 80°C, then acidified with 6M HCl (20 mL, 120 mmol), and a solution of $Eu(NO_3)_3.4H_2O$ (2.23^^g, 5.0mmol) in water (10mL) was added. The solution pH was adjusted to 7-8 by the addition of CsOH (10g) in water (50mL). The resultant precipitate was isolated by filtration (22.0g) and a portion (2.0g) was recrystallized

from water to yield colorless plates of **2**. Yield: 0.48g (24% based on W). Elemental analysis (%) calcd: Cs 18.54, Na 1.13, Eu 4.78, W 52.01, As 2.35; found: Cs 18.53, Na 0.98, Eu 4.60, W 50.20, As 2.24. IR (KBr disk): υ=941 (m), 885 (s), 793 (m), 710cm^{-1} (s).

Compounds **1** and **2** were also obtained by the reaction between the [α-AsW_9O_{33}]$^{9-}$ ligand and the Ln^{3+} ion in an aqueous solution containing alkali-metal cations: For **2**, solid CsCl (0.50g, 2.9mmol) was added to a solution of $Na_9(\alpha\text{-}AsW_9O_{33}).19.5H_2O$ (1.4g, 0.50mmol)[13] and $Eu(NO_3)_3.6\hat{}H_2O$ (0.22g, 0.50mmol) in water (55mL) at pH6.2. The solution was warmed to approximately 80°C for 30min then cooled to room temperature to yield a white precipitate. After isolation of the crude product by filtration, a portion (1.0g) was recrystallized from a solution of CsCl (0.2g, 1.2mmol) in water (30mL) with a yield of 0.16g

For **2** a total of 67961 reflections (ω scan and $2\theta_{max}$=55.4°) was collected of which 67408 unique reflections (R_{int}=0.085) were used. Crystal data: M_r=12726.30, Space group P1 (No.2), a=20.386(1), b=28.100(2), c=35.258(1)Å, α=101.113(4), β=102.605(1), γ=98.733(2)°, Z=4, V=18940.7(2)Å^3, ρ=4.46g cm^{-3}, μ=272.6cm^{-1}, F(000)=21896. Crystal size=0.16x0.10x0.03mm. Transmission factors of 0.03-0.25. The structure was solved by a direct method (SHELXS-97)[15] and refined based on 67408 observed all reflections (with I>0.0σ(I) and 2527 parameters) to R_1=0.111 (refined agains /F/) for I>2σ(I) and R_w=0.304 (refined against /F^2/) for I>0.0σ(I). The highest residual

electron density 6.6e $Å^{-3}$. All calculations were performed using the CrystalStructure software package(*CrystalStructure 3.00*:*Crystal Structure Analysis Package*, Rigaku and Rigaku/MSC **2000**--**2002**) except for refinement, which was performed using SHELXL-97. The site occupancies of Na13 and Cs30-Cs47 atoms were fixed at 1/2 for the most reasonable temperature factors for all the Na and Cs atoms after several least-squares refinements.