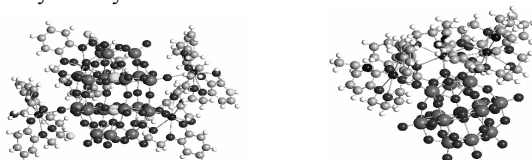


DB18C6 Sodium Polyoxometalate Supramolecular Complexes With α -Dawson and α -Keggin Structure

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Since 1996, Lu et al have reported a series of supramolecular complexes containing polyoxometalates and crown ethers.¹ In this paper, continuing our work, we describe two novel crown ether sodium heteropolyoxometalate supramolecular complexes obtained by solvothermal reaction and characterized by X-ray, IR, UV-vis, multinuclear NMR and gUMBC NMR.

As shown in the Figures, $[\text{Na}(\text{DB18C8})(\text{H}_2\text{O})]_4[\text{X}_2\text{M}_{18}\text{O}_{62}]$ ($\text{X}=\text{S}$, $\text{M}=\text{Mo}, \text{W}$) (**1**) consists of four dibenzo-18-crown-6 (DB18C6) sodium complex cations and one α -Dawson heteropolyoxometalate, while $[\text{Na}(\text{DB18C8})(\text{CH}_3\text{CN})]_3[\text{XM}_{12}\text{O}_{40}]$ ($\text{X}=\text{As}$ and P , $\text{M}=\text{Mo}$ and W) (**2**) consists of three DB18C6 sodium units and an α -Keggin heteropolyanion. Each sodium ion is located in the cavity of DB18C6, and the four $[\text{Na}(\text{DB18C8})]^+$ ions in **1** are linked to four terminal O atoms from two "belt" layers of the Dawson-type polyanion, while the three complex cations in **2** are bound to terminal O atoms from one M_3O_{13} unit of the α -Keggin structure. The effects dominating the self-assembly of the two types of supermolecules are charge compensation and higher symmetry.



$[\text{Na}(\text{DB18C8})(\text{H}_2\text{O})]_4[\text{S}_2\text{Mo}_{18}\text{O}_{62}]$ $[\text{Na}(\text{DB18C8})(\text{CH}_3\text{CN})]_3[\text{PMo}_{12}\text{O}_{40}]$

[1] Lu X.M., Zhong R.F., Liu S.C., Liu Y., *Polyhedron*, 1997, **16**, 3865.

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