Rare holmium, thulium and lutetium-octamolybdate $[Mo_8O_{28}]^{8-}$ 1D chains

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Introduction & research goal

Polyoxometalates (**POMs**) are discrete anionic metal-oxygen clusters of early transition metals usually W, Mo, or V in a high oxidation state. [1] One of the most fascinating lanthanide POMs (LnPOMs) is the $(NH_4)_{12}H_2(Eu_4(MoO_4)(H_2O)_{16}(Mo_7O_{24})_4)\times 13H_2O$ cluster reported by Nakamura et al.[2] This LnPOM showed very good anti-HIV-1 activity, anti-bacterial activity on several different cell lines, as well as very good luminescence properties.

Polyoxometalates

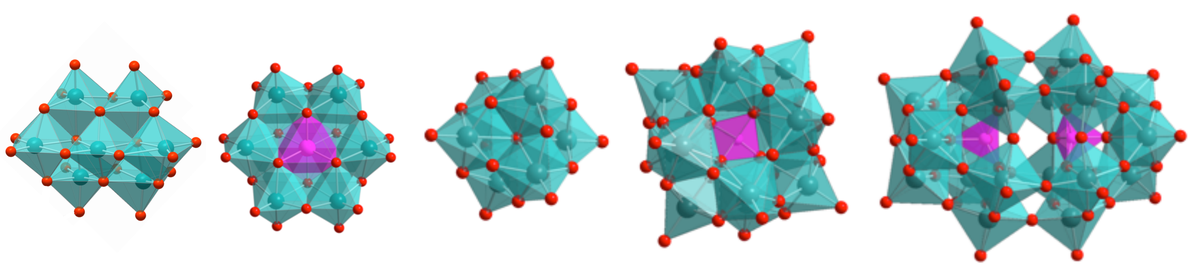

Fig. 1: *POMs exhibit a huge variety in their size, shape and nuclearities. From left to right structures of some common POMs: heptamolybdate, Anderson-Evans, Lindqvist, Keggin and Wells-Dawson POMs.[2]*

Earlier we have reported a series of tetranuclear LnPOMs built from $[Mo_7O_{24}]^{6-}$ heptamolybdate polyanions with La^{3+}, Eu^{3+}, Tb^{3+}, Sm^{3+}, Dy^{3+}, and Nd^{3+} were synthesized and a detailed analysis revealed that the tetranuclear clusters formed monomers or dimers linked through oxygen bridges.[3] The smaller lanthanide ions - Er^{3+} and Yb^{3+} did not form tetranuclear clusters, but instead mononuclear sandwich type POMs were obtained. For other lanthanides with a smaller ionic radius - **Ho^{3+}**, **Tm^{3+}** and **Lu^{3+}** no crystals could be obtained in those conditions. Only when doubling the amount of the lanthanide salt, single crystals suitable for data collection were obtained. Surprisingly, the 1D chains no longer comprise of the $[Mo_7O_{24}]^{6-}$ units, but of **$[Mo_8O_{28}]^{8-}$** instead. Two types of **octamolybdate anions** can be found in literature: $[Mo_8O_{26}]^{4-}$ and the mentioned above $[Mo_8O_{28}]^{8-}$.[3-5] The existence of compounds built of the $[Mo_8O_{26}]^{4-}$ unit is much more common. $[Mo_8O_{26}]^{4-}$ has eight isomers: α, *β*, *γ*, *δ*, *ε*, *ζ*, η, θ, where each of these isomers can be viewed as distorted arrays of cubic close-packed oxygen atoms with Mo atoms occupying the interstitial sites. To the best of our knowledge this is a **rare example of compounds built from the $[Mo_8O_{28}]^{8-}$ unit and the first series of compounds with this POM unit built from lanthanide ions.**

Crystal structure of LuPOM

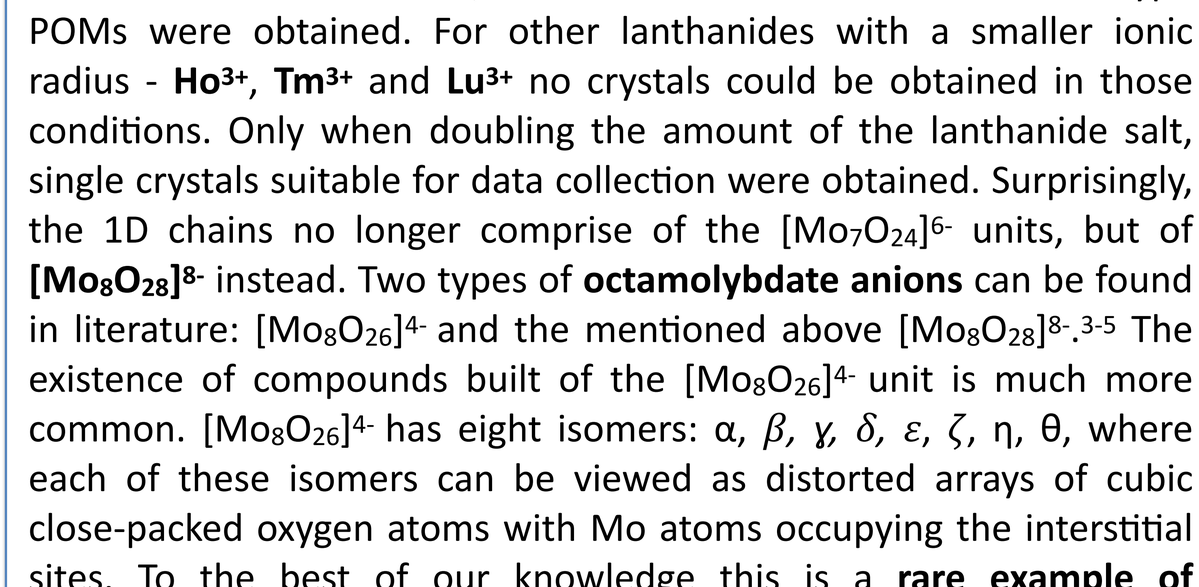

Fig. 2: *1D polymeric chain of **$[Mo_8O_{28}]^{8-}$** units, connected through shared oxygen atoms, along the [101] direction. Every second **$[Mo_8O_{28}]^{8-}$** unit is linked to two eight-coordinated Lu^{3+} ions.*

References

1. Pope, M. T.; Müller, A., *Angew. Chem. Int. Ed.*, **1991**, *30*, 34-48.
2. Ma, X.; Yang, W.; Chen, L.; Zhao, J. *CrystEngComm*, **2015**, *17*, 8175-8197.
3. Kaczmarek, A.M., Van Hecke, K., Van Deun, R. *Inorg. Chem.*, **2017**, 56, 3190-3200.

Crystal structure of LuPOM

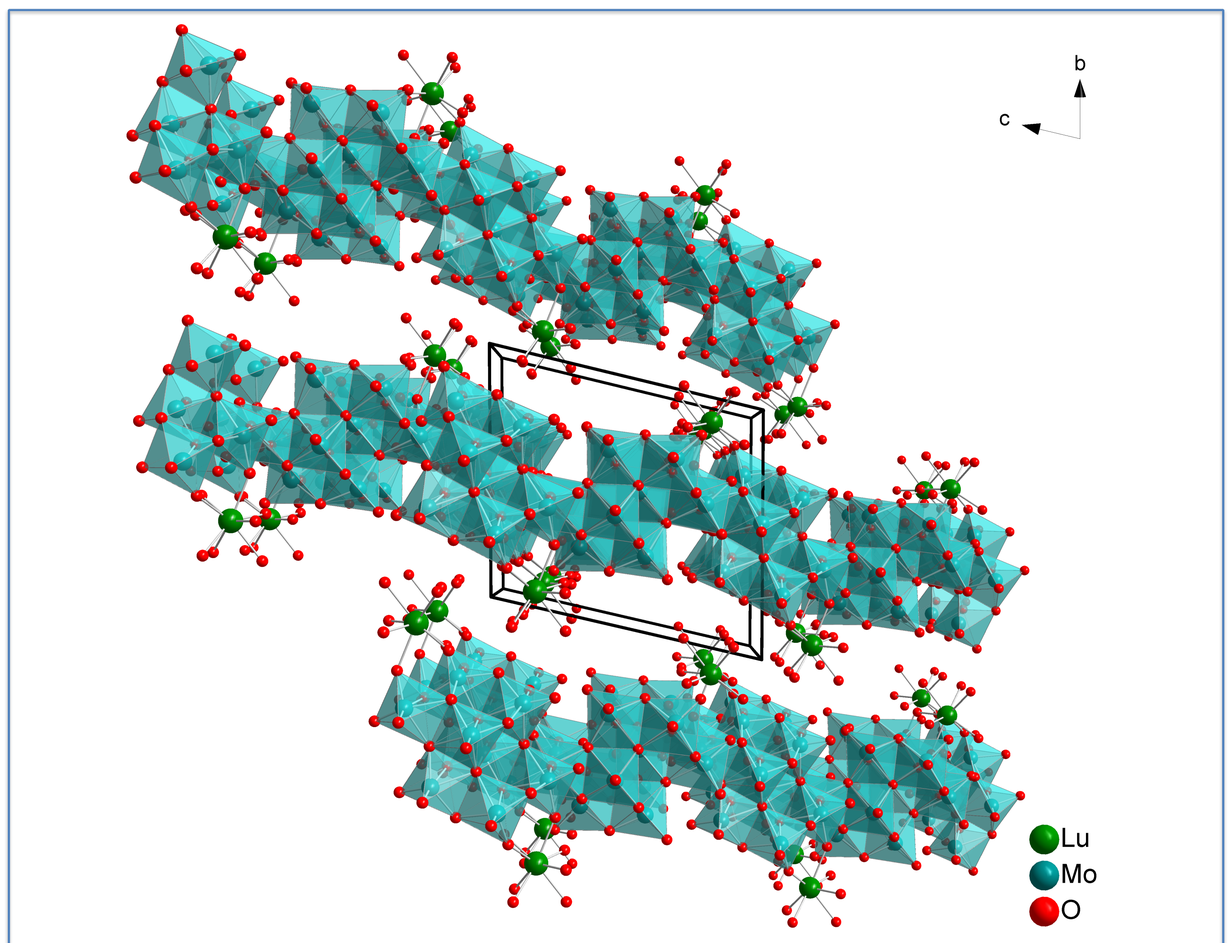

Fig. 3: *Perspective packing diagram in the crystal structure of the Lu^{3+} **$[Mo_8O_{28}]^{8-}$** LuPOM compound, showing the 1D polymeric chains of **$[Mo_8O_{28}]^{8-}$** units, parallelly lined up in the same (010) planes.*

Luminescence properties of Eu: LuPOM

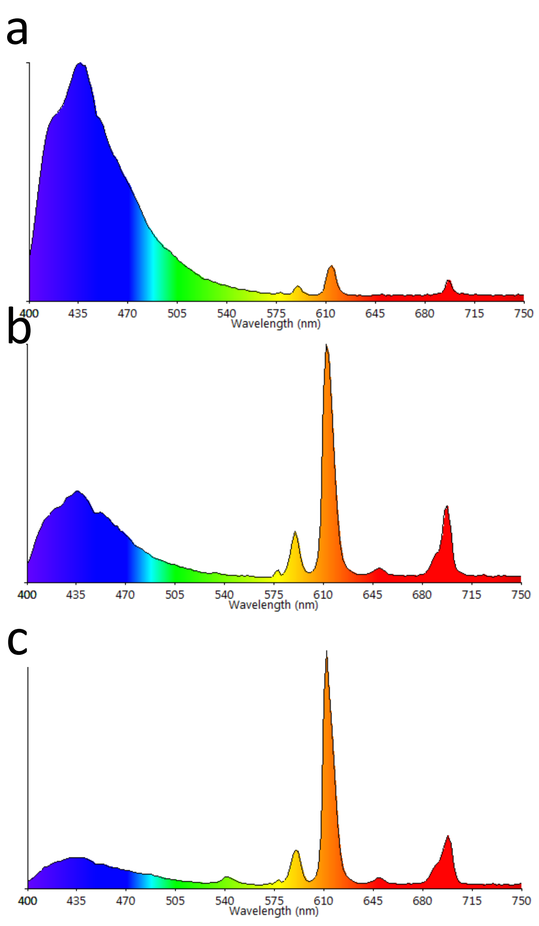

Fig. 4: *Emission spectra with rainbows fitted underneath the curve of a) 1% Eu: LuPOM, b) 2.5% Eu: LuPOM, and c) 5% Eu: LuPOM (in all cases the emission spectrum was recorded when exciting into the maximum of the LMCT band).*

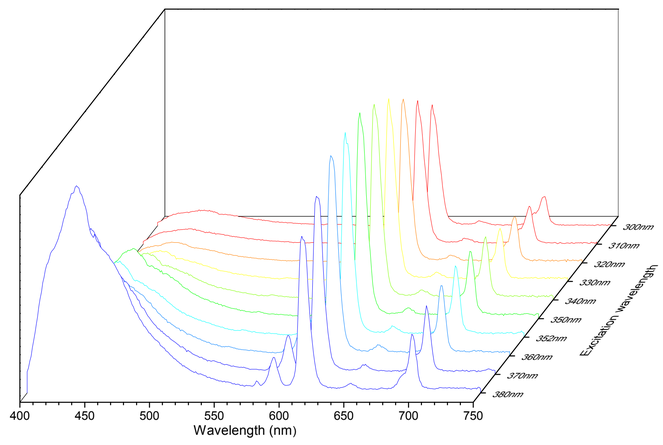

Fig. 5: *Emission map for 2.5%Eu: LuPOM excited at different wavelengths (300 – 380 nm); the spectra were observed at the maximum of the $^5D_0 \rightarrow {}^7F_2$ transition peak.*

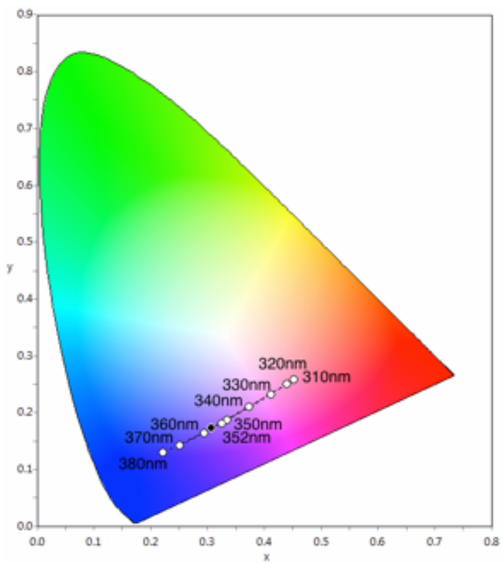

Fig. 6: *CIE color diagram for 2.5%Eu: LuPOM*

Conclusion

We report a novel series of 1D chain like structures built from the $[Mo_8O_{28}]^{8-}$ POM units obtained for Ho^{3+}, Tm^{3+}, and Lu^{3+}. To the best of our knowledge this is a rare example of compounds built from the $[Mo_8O_{28}]^{8-}$ unit and the first series of compounds with this POM unit built from lanthanide ions. Also they are among the few examples of 1D chain like structures built from POM units reported in literature. The LuPOM compound could be doped up to 7.5% percentage with Eu^{3+} ions without changing the structure yielding red or varying orange/pink to dark blue emission color.