Anion influence over the nuclearity of $\{M(MeOsalR)\}_x\{KA\}_y$ (R= en, pr, ph; A= PF_6^-, NO_3^-, NCS^-, Br^-, I^-) species.

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Abstract:

The bicompartmental *salen* ligands are widely explored due to their applications [1] and versatility, because they can introduce different types of ions in their two cavities, a N_2O_2 inner core suitable for **3d** metal ions and an outer compartment O_2O_2 that can fit alkali or alkali-earth ions (Figure 1). These species can mimic biomolecules responsible for the selective transport of ions. They present several topologies and dimensionality depending on the nature of the metal ions, on the counter-anion coordinative ability and on the length of the bridge between the nitrogen atoms [2-5].

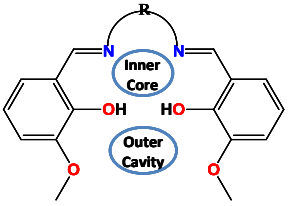


Figure 1. Bicompartmental Schiff-base ligand H_2MeOsalR.

We have characterized several complexes with these kind of ligands containing **Ni(II)** or **Cu(II)** ions in the inner core and **K(I)** in the outer cavity and introducing different counter anions such as PF_6^-, NO_3^-, NCS^-, Br^- and I^-. The compounds present high structural diversity with several stoichiometries **M**:**K(I)** (Figure 2):

- **1:1:** Compounds with this stoichiometry give rise to mainly **discrete units** like [Cu(MeOsalen)KPF_6].
- **2:1:** In these complexes the potassium ion is linked to the external cavity of two different bicompartmental ligands, which can be sited inside (Fig.2a), $[\{Ni(MeOsalph)\}_2K(NCS)]$, or outside (Fig.2b) the external compartment (***double-decker sandwich***), $[\{Ni(MeOsalen)\}_2K(PF_6)]$. Depending on the distinct interactions and the crystallization conditions can be obtained different **polymorphs**, like $[\{Cu(MeOsalpr)\}_2K(PF_6)]$ compounds.
- **3:2:** The only examples obtained appear when the anion is PF_6^-. They show the two potassium ions located between the outer compartments of two ligand units (***triple-decker sandwich***), like in $[\{M(MeOsalph)\}_3\{KPF_6\}_2]$ (M= Ni(II), Cu(II)) or $[\{Ni(MeOsalpr)\}_3\{KPF_6\}_2]$.
- **6:5:** This stoichiometry is only present in compounds with NCS ions, which are coordinated to the potassium ions (***multi-sandwich***), like in $[\{M(MeOsalen)\}_6\{K(NCS)\}_5](H_2O)_4$.
- **Polymers:** They correspond to linear chains with different stoichiometries depending on the counter anion present, **1:1** like in [Ni(MeOsalen)K(NCS)(DMF)] and [Ni(MeOsalpr)KI], or **2:1** like $[\{Cu(MeOsalen\}_2KBr]$.

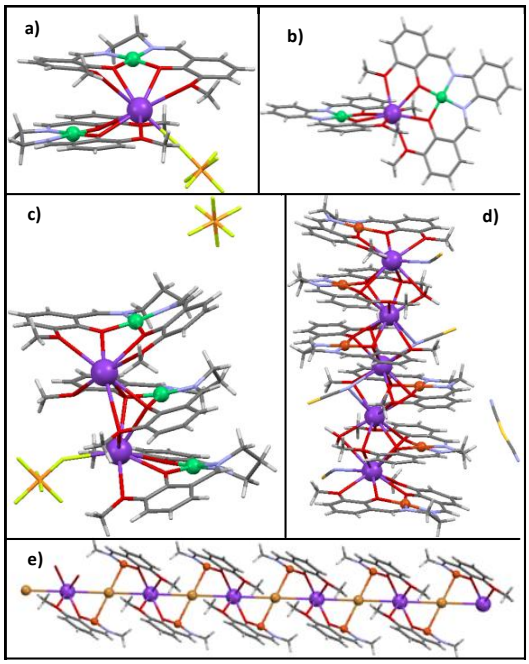


Figure 2. Different structural types: a) **2:1** $[\{Ni(MeOsalen)\}_2K(PF_6)]$; b) **2:1** $[\{Ni(MeOsalph)\}_2K(NCS)]$; c) **3:2** $[\{Ni(MeOsalpr)\}_3\{KPF_6\}_2]$; d) **6:5** $[\{Cu(MeOsalen)\}_6\{K(SCN)\}_5](H_2O)_4$; e) **polymer** $[\{Cu(MeOsalen\}_2KBr]$.

Recent Publications:

1. Cozzi PG (**2004**) Metal–Salen Schiff base complexes in catalysis: practical aspects. *Chem. Soc. Rev*. **33:410-421**.
2. Mousavi M, Bereau V, Costes JP, Duhayon C, Sutter JP (**2011**) Oligomeric and polymeric organizations of potassium salts with compartmental Schiff-base complexes as ligands. *CrystEngComm.* **13:5908–5914**.
3. Biswas A, Mondal S, Mohanta S (**2013**) Syntheses, characterizations, and crystal structures of 3d–s/d10 metal complexes derived from two compartmental Schiff base ligands. *J. Coord. Chem*. **66(1):152-170.**
4. Sasmal S, Majumder S, Hazra S, Sparkes HA, Howard JAK, Nayak M, Mohanta S (**2010**). Tetrametallic [2 × 1 + 1 × 2], octametallic double-decker–triple-decker [5 × 1 + 3 × 1], hexametallic quadruple-decker and dimetallic-based one-dimensional complexes of copper(II) and s block metal ions derived from *N*,*N*′-ethylenebis(3-ethoxysalicylaldimine). *CrysEngComm.* **12:4131-4140.**
5. Finelli A, Herault N, Crochet A, Fromm KM (**2018**) Threading Salen-type Cu- and Ni-Complexes into One-Dimensional Coordination Polymers: Solution versus Solid State and the Size Effect of the Alkali Metal Ion. *Cryst. Growth Des.* **18: 1215–1226.**

Biography:

Jesús Tapiador Cebrián is a 2nd year PhD student at the department of Inorganic Chemistry of “Universidad Complutense de Madrid”, Spain. His current research is carried out into the “Molecular and polymers materials based on coordination compounds” and is focused on the chemistry of polinuclear coordination derivatives based on Schiff- base ligands and the study of their magnetic and optical properties as well as their structural characterization by single crystal X-Ray Diffraction.

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