**Small Cause — Great Effect: What the 4fn+15d0 → 4fn5d1 configuration crossover does to the chemistry of divalent rare-earth halides and coordination compounds, and how it makes the formation of cluster complex compounds and polar intermetallics possible**

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The rare-earth elements in the divalent state, i.e. with oxidation number +2, may either have the electron configuration 4fn+15d0 (symbolized as *R*2+) or 4fn5d1 (*R*3+e-). As *R*2+ (*R* = Eu, Yb, Sm, Tm, Dy, Nd) they can either be contained in extended solids as in the insulating diiodides *R*I2, or in coordination complexes such as samarocene, Kagan’s reagent, or TmI2(DME)3, Fig. 1. In the case of *R*3+e-, the “excess” d electron can either be delocalized and cause (semi)metallic behavior in extended solids, e.g. in LaI2, or localized with the *R*3+e- = 4fn5d1 ion trapped in a coordination complex with (super)bulky ligands such as in [K(2.2.2-crypt)][LaCp”3]. Thus, the seemingly small cause of a one-electron configuration crossover, 4fn+15d0 ↔ 4fn5d1 has a large effect on the chemical behavior and physical properties of the respective compounds where atomic properties and ligand effects play important roles [1].

**Fig. 1.** Rare-earth elements *R* exhibiting the oxidation state +2 under ambient conditions as diiodides, *R*I2, (left) and in coordination compounds (right) with their respective electron configurations: Highligthed in blue: 4fn+15d0, and in red: 4fn5d1.

 In the solid state, dihalides with *R* in the 4fn5d1 configuration (including *R* = Y, Tb, Ho, Er, Lu) compete with cluster complex halides, {*Z*z*Rr*}*X*x, or polar intermetallics, {*Z*z*Rr*}. In both cases, *Z* atoms center an *R*r cluster. The endohedral atom *Z*, either non- or semi-metal (*Z* = *E*) or (transition) metal atom (*Z* = *T*) is mandatory for heteroatom *Z−R* bonding. So far, {*Z*z*R*r}*X*x type compounds are known with *r*, i.e. the coordination number (CN) of the endohedral atom, ranging from 3 to 8. Smaller atoms like *E* = B, C, N, O afford smaller CN’s (3*−*6), while larger atoms like *T* = Os (and many other transition metal atoms) demand CNs of 6 to 8 [2, 3].

 Bonding in these cluster complex halides {*Z*z*R*r}*X*x is predominantly a symbiosis of polar, heteroatomic *Z─R* (intermetallic-like, multi-center covalent) and *R─X* (salt-like, ionic) character. Increasing cluster condensation pushes isolated clusters into oligomers, chains, double chains, then layers and, finally, three-dimensional structures. Ultimate cluster condensation, at which end all the halide ligands are eliminated, constitutes polar intermetallics.

When the electronegativity of the halide increases, there is an increasing competition of cluster complex halide *versus* intermetallic and salt. For example, when {PtPr3}Cl3 was targeted, the intermetallic {Pt3Pr4} as well as remaining PrCl3 was obtained, the latter apparently working as a flux for crystal growth. Although the system Pt/Pr seems to have been investigated thoroughly, the new Pt3Pr4 does not exist in the phase diagram [4]. Other fluxes, such as sodium chloride instead of PrCl3 or tin melts, resulted in the formation of what might be considered as a new modification of Pt2Pr3 and a number of ternary Pt/Sn/Pr intermetallics [5].

**References**

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