SP2. Synthesis of High-Spin Dendritic Bis(oxamato) Bridged Complexes

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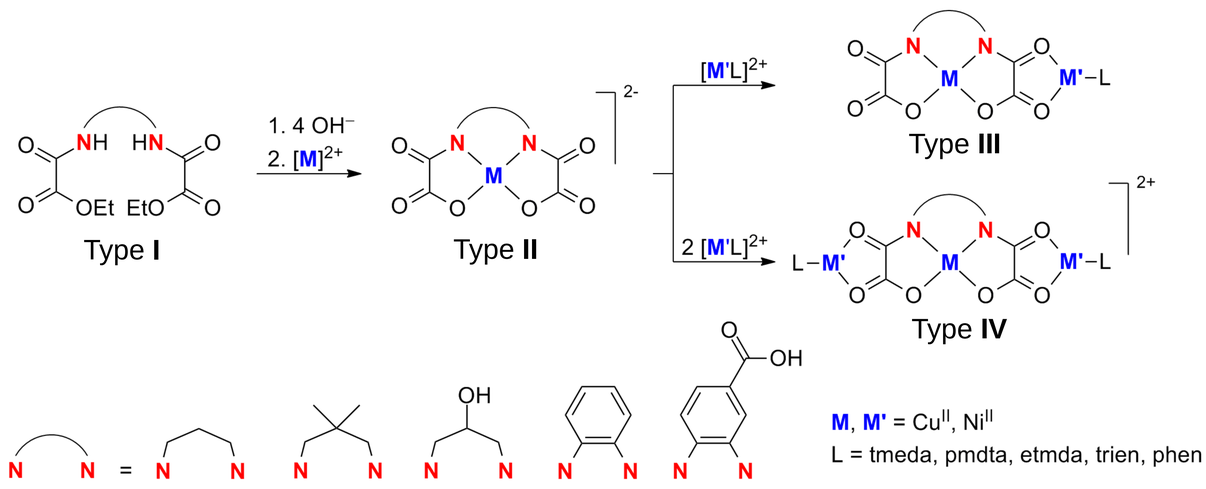
Motivation

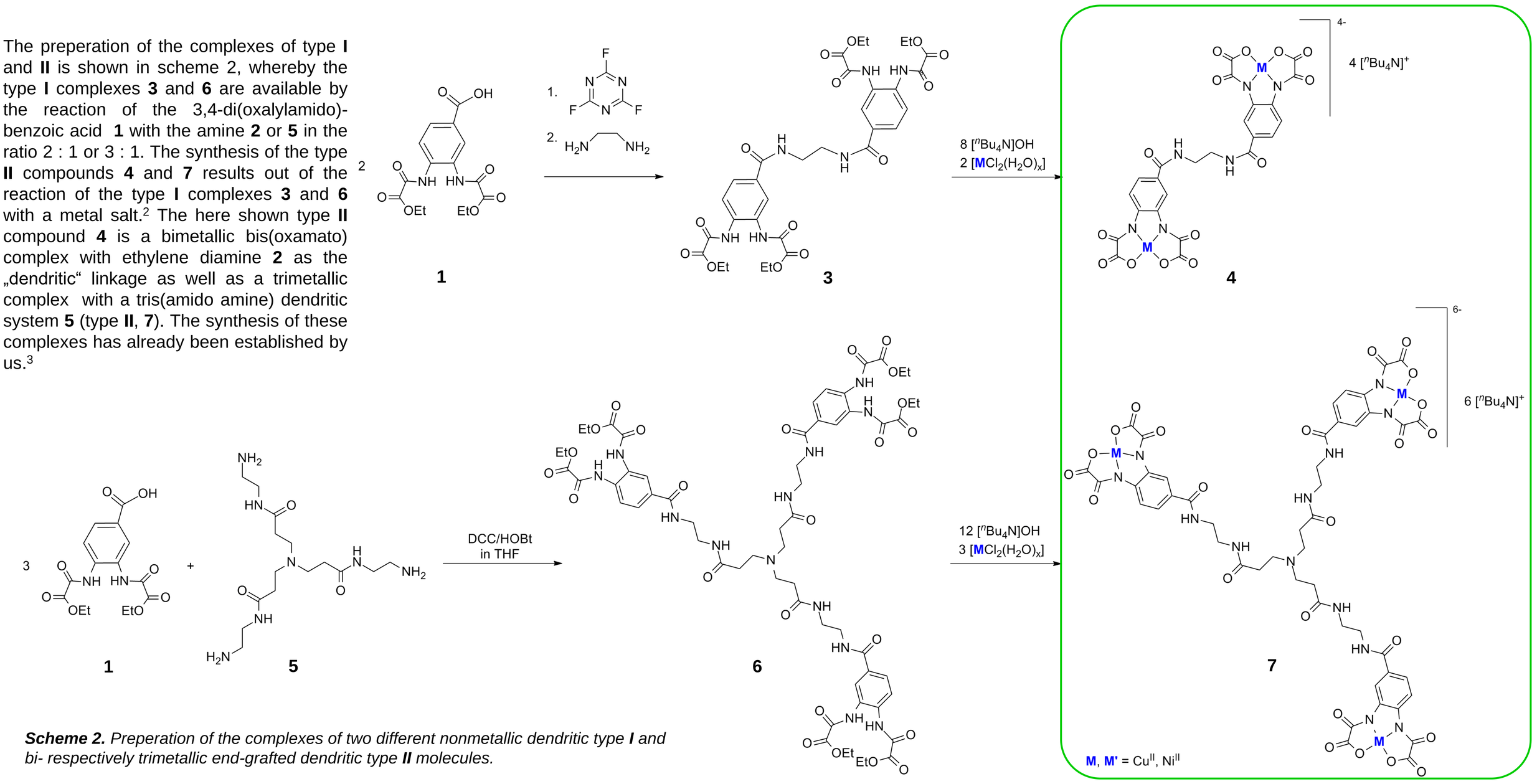
One possibility to cover the persistent demand of magnetic materials is the development of those molecular-based materials. In this context polymetallic bis(oxamato) bridged complexes have already been synthesized (scheme 1). Based on type **I** molecules type **II** complexes could be generated possessing flexidentate properties. The last named can be used for the synthesis of even bi- (type **III**) or trimetallic (type **IV**) systems (scheme 1). Molecules of type **III** and **IV** show properties similar to these of paramagnetic, multimetallic complexes in which adjacent metal ions possess an intramolecular antiferromagnetic exchange. Considering this background polymetallic, dendritic complexes with end-grafted bis(oxamato) units became of interest. This family of molecules could afford many applications (i.e. use in homogeneous catalyses showing dendritic effects). The occurrence of dendritic effects affects the chemical and physical properties, which again show a dependence by changing the generation of the dendritic systems.[1]



Scheme 1. *Basic chemical structures of type **I** molecule and **II** – **IV** complexes.*

Preliminary Results

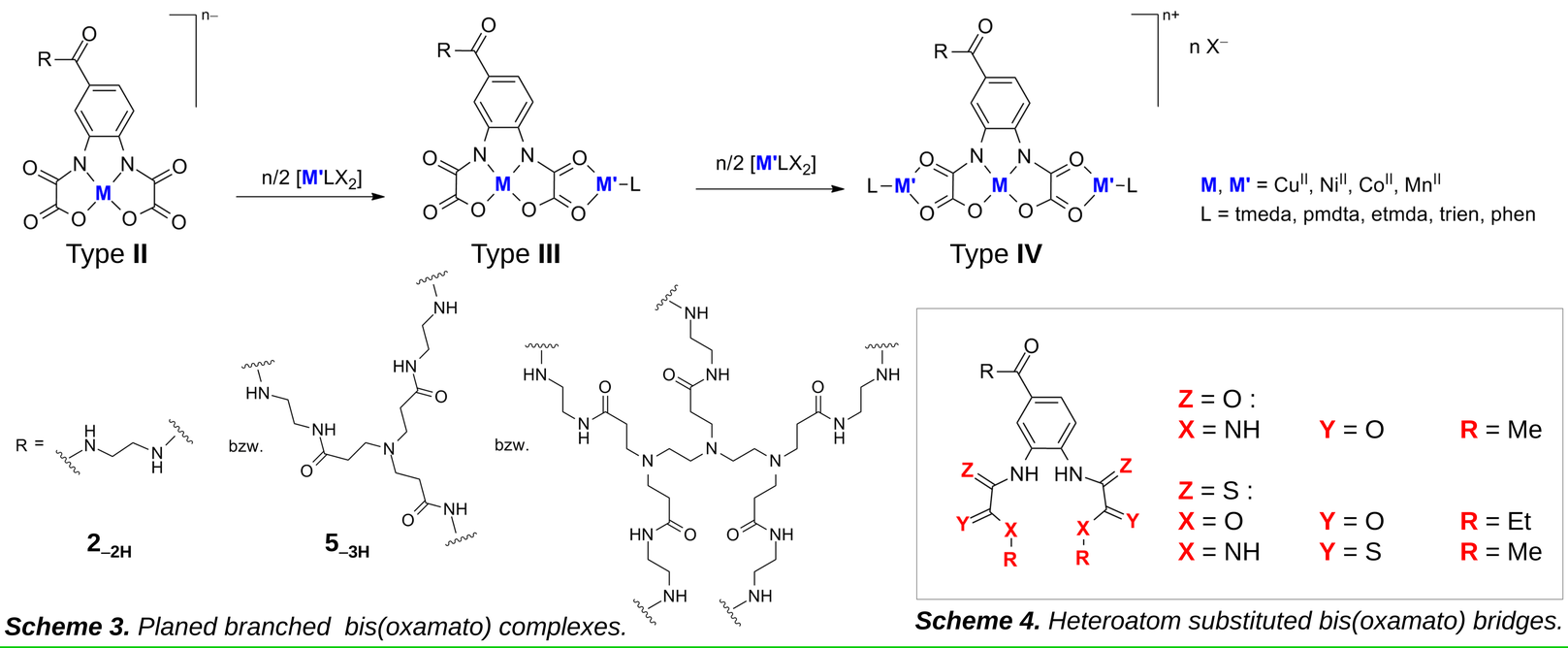
The preperation of the complexes of type **I** and **II** is shown in scheme 2, whereby the type **I** complexes **3** and **6** are available by the reaction of the 3,4-di(oxalylamido)-benzoic acid **1** with the amine **2** or **5** in the ratio 2 : 1 or 3 : 1. The synthesis of the type **II** compounds **4** and **7** results out of the reaction of the type **I** complexes **3** and **6** with a metal salt.[2] The here shown type **II** compound **4** is a bimetallic bis(oxamato) complex with ethylene diamine **2** as the „dendritic“ linkage as well as a trimetallic complex with a tris(amido amine) dendritic system **5** (type **II**, **7**). The synthesis of these complexes has already been established by us.[3]



Scheme 2. *Preperation of the complexes of two different nonmetallic dendritic type **I** and bi- respectively trimetallic end-grafted dendritic type **II** molecules.*

Outlook

Starting from type **II** complexes several type **III** and **IV** complexes shall be prepared. Therefore transition metal complex fragments will be added to the type **II** compounds **4** and **7** like e.g. $[Cu(L)]^{2+}$ (L = pmdta, bipy, phen) in order to obtain dendritic molecules which are end-grafted with two- or trimetallic bis(oxamato) units (scheme 3). Further shall be investigated how a heteroatom substitution of the oxamato bridges will influence e.g. the antiferromagnetic couplings (scheme 4).[4,5] Anymore dendritic systems of higher generations as linkages between the bis(oxamato) units shall be investigated.



Scheme 3. *Planed branched bis(oxamato) complexes.*

Scheme 4. *Heteroatom substituted bis(oxamato) bridges.*

Characterization & Intentions

- IR and Raman spectroscopy
- ESR spectroscopy
- Magnetic measurments by SQUID magnetometry
- Formation of thin films by spin coating on different surfaces
- Magneto-optical characterization by MOKE spectroscopy

Prove of dendritic effects with respect to the magnetic properties

References & Acknowledgment

[1] Fritz Vögtle, Gabriele Richardt, Nicole Werner, Dendritische Moleküle Konzepte, Synthesen, Eigenschaften, Anwendungen, 1. Auflage, Teubner Verlag, Wiesbaden, 2007.
[2] François Eya’ane Meva, *Dissertation*, TU Chemnitz 2009.
[3] Robert Mothes, *Diplomarbeit*, TU Chemnitz 2008.
[4] Rafael Ruiz et al., *J. Chem. Soc., Dalton Trans.*, **1997**, 745.
[5] Mohammad A. Abdulmalic, ongoing dissertation.

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