SP2. Synthesis of Multimetallic High-Spin Complexes & Transition Metal Carboxylates

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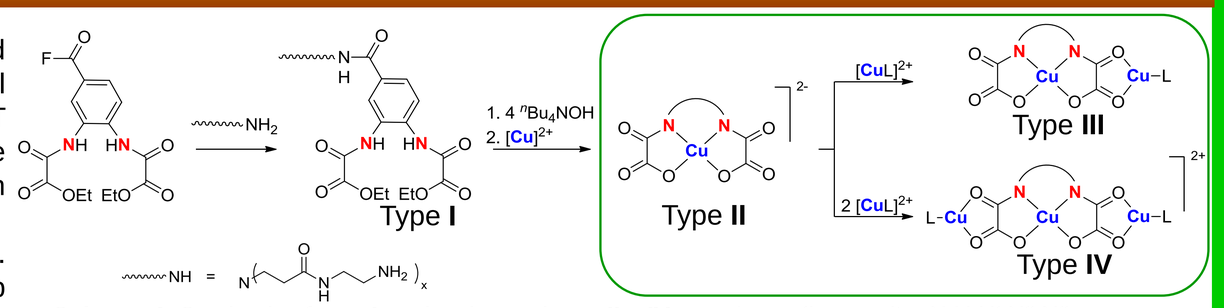
Introduction

A high number of trimetallic Cu(II) bis(oxamato) type complexes (Scheme 1) have been synthesized and characterized. Magnetic measurements have been carried out. For five-coordinated terminal Cu(II) ions (type **III** and **IV**; for example L = pmdta) of trinuclear bis(oxamato) type complexes the $\chi_m T$ value decreases with lowering the temperature, indicating an antiferromagnetic coupling between the paramagnetic Cu(II) ions. Typically *J* values for oxamato bridged trinuclear Cu(II) complexes with tridentate amines as terminal ligands are between –84 to –196 cm^{-1}[1].
Considering this it is obvious to generate systems within more than one metalated bis(oxamato) unit. Because PAMAM-based dendritic systems are established and well understood in our working group these systems shall be endgrafted with bis(oxamato) units to give multimetallic high-spin complexes.



Scheme 1. *Synthesis of type **I** molecules and type **II** – **IV** complexes (L = pmdta; N,N,N‘,N“,N“-pentamethyldiethylentriamine) [2, 3].*

Preliminary Results

Multimetallic High-Spin Complexes

Within this work type **III** and **IV** complexes could be prepared which are linked by ethylendiamine (**a**) and „dendritic“ systems (**b** and **c**). For the linkage, PAMAM-based dendritic systems have been used containing three or five amines as terminal groups.

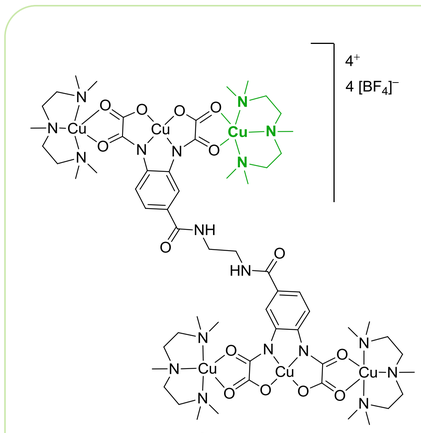
The products have been characterized by ESI-MS measurements (Figures 1 – 3). For all complexes the measured ESI-MS (Electrospray Ionization Mass spectrometry) spectra fit well with the calculated ones.

ESI-MS-Spectra

ESI-MS spectra were measured for type **III/IV** and **IV** complexes (Figures 1 – 3), whereby complex type **III/IV** signifies a mixture of the explained type **III** and **IV** species. After reaction of the dinuclear Cu(II) complex of type **II** with [Cu(pmdta)$(BF_4)_2$], type **III/IV-a** and **IV-a** complexes were formed. The occurrence of a type **III/IV** complex may indicate that a complete metallation of the terminal sides is not achieved. Furthermore, it cannot be ruled out that due to the method of the ESI-MS measurement fragmentation did occur.

After the reaction of the higher type **II** complexes with [Cu(pmdta)$(BF_4)_2$] ESI-MS measurements show always the appearance of type **III/IV** complexes. Pure type **IV** complexes could not be detected which may be a reason of fragmentation as mentioned before or incomplete substitution.

We could show that we are able to synthesize the dendritic bis(oxamato) type **III/V-a,b,c** and **IV-a** complexes and coordinate them to Cu(II) complex fragments with up to 12 and 13 unpaired electrons (**III/IV-c**).



III/IV-a + **IV-a**

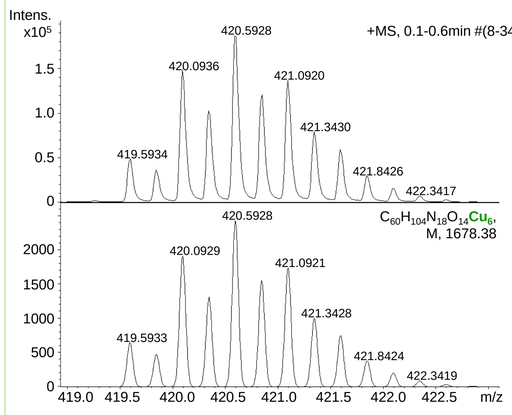
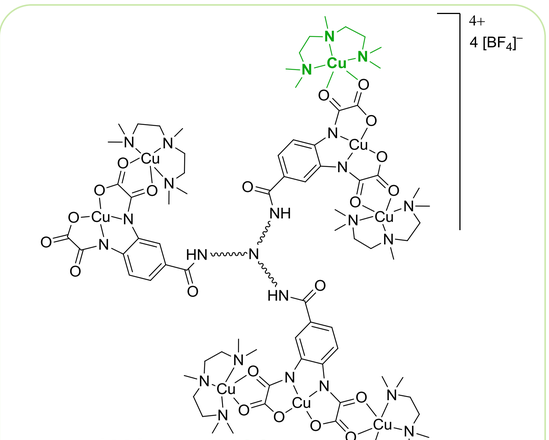


Fig. 1. *ESI-MS spectra of **IV-a** containing six Cu(II) ions (upper part: measured peak, lower part: calculated peak). A further peak could be observed showing a complex of type **III/IV** containing five Cu(II) ions.*



III/IV-b + **III/IV-b’**

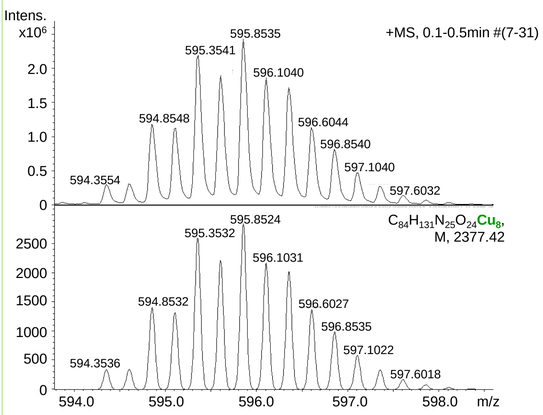
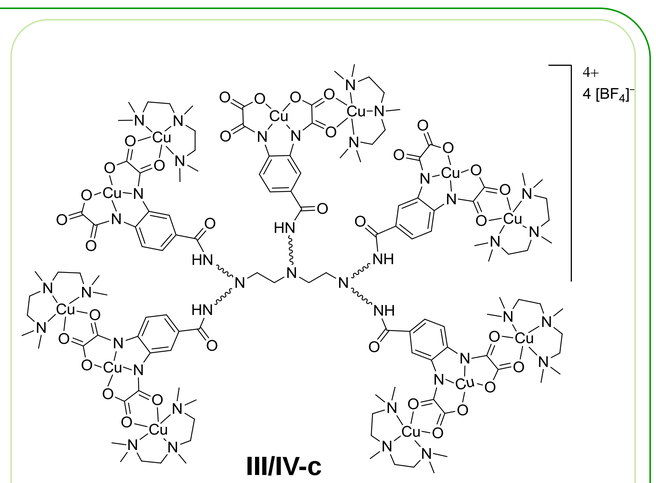


Fig. 2. *ESI-MS spectra of **III/IV-b’** containing eight Cu(II) ions. Further peaks could be detected showing the existence of molecules featuring seven Cu(II) ions (**III/IV-b**).*



III/IV-c

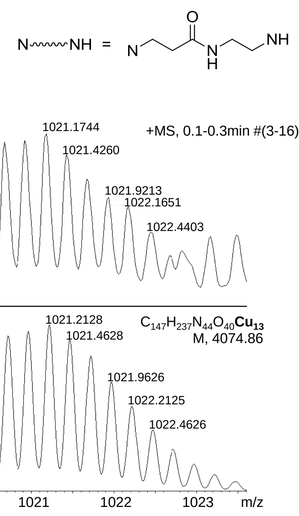
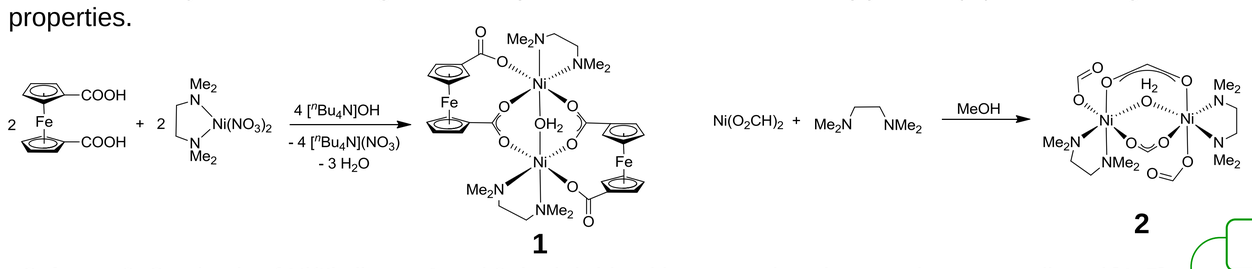


Fig. 3. *ESI-MS spectra of **III/IV-c**, containing 13 Cu(II) ions. Another peak could be detected corresponding to 12 Cu(II) ions.*

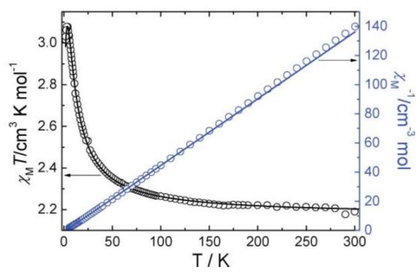
Transition Metal Complexes

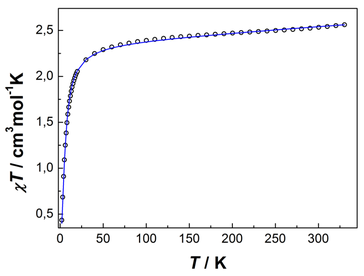
The Ni(II) complexes **1** and **2** shown in Scheme 2 have been invested in our working group [4,5]. For both complexes the solid-state structure could be determined. The ferrocene containing molecule **1** shows also a ferromagnetic coupling between the Ni(II) ions of J = 2.2 cm^{-1} (Fig. 4). The Ni(II) formate complex **2** shows a weak antiferromagnetic coupling of J = –1.62 cm^{-1} despite its similar structural conformity to complex **1** (Fig. 4).
Furthermore the presence of the two ferrocenyl substituents in **1** motivated us to study the spectro-electrochemistry and to investigate the impact of the oxidation of Fe(II) to Fe(III) to the magnetic properties.



1 **2**

Scheme 2. *Synthesis of Ni(II) dimers **1** and **2**, both bridged by two carboxylates and one water ligand* [4, 5].





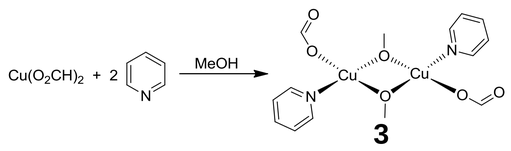
Spin-Hamiltonian used for **2**:

$$\hat{H} = -2J\hat{S}_1\hat{S}_2 + \sum_{i=1}^{2} g_i \mu_B \hat{S}_{i\tau} B_\tau$$

$$(\tau = x, y, z)$$

Fig. 4. *Plot of χ_M^{-1} and $\chi_M T$ vs. T for **1** (left) and **2** (right). Circles: experimental values, solid line: theoretical curve* [5].

Carboxylato bridged complexes could be a further possibility for obtaining discrete polynuclear complexes and/or coordination polymers indication magnetic interactions. Scheme 3 shows the synthesis of an mathanolate-bridged Cu(II) complex which crystallizes in a polymeric structure which can be understood as beeing formed from dinuclear entities of **3** (Fig. 5). The magnetic measurement has been carried out but the results are not completely interpreted until now.



3

Scheme 3. *Synthesis of Cu(II)-dimer **3** bridged by two methanolate ligands.*

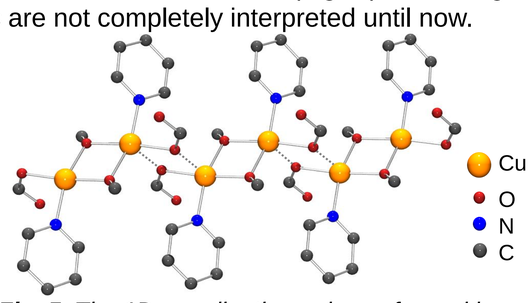
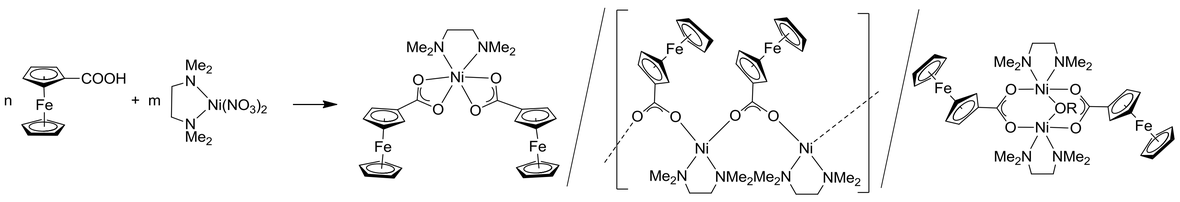


Fig. 5. *The 1D coordination polymer formed by entities of the Cu(II)-dimer **3** in the solid state.*

Outlook

Further carboxylato bridged coordination polymers will be synthesized. For this, Cu(II), Ni(II), Co(II) and Mn(II) formates will be used as shown in the reactions of **2** and **3** (Scheme 2 and 3). Some Cu(II) coordination polymers have already been synthesized in our working group and their magnetic behavior has to be investigated now. Further compounds with ferrocene carboxylic acid as a bridging ligand will be synthesized. One reaction has already been carried out as shown in Scheme 4.



Scheme 4. *Proposed structures of the products of the reaction from ferrocene carboxylic acid with [Ni(tmeda)$(NO_3)_2$] (tmeda = N,N,N’,N’-tetramethylethylenediamine) [4, 6, 7].*

References & Acknowledgement

[1] T. Rüffer, B. Bräuer, A. K. Powell, I. Hewitt, G. Salvan, *Inorg. Chim. Acta*, 360, **2007**, 3475. [2] F.E. Meva, *Dissertation*, TU Chemnitz **2009**. [3] Robert Mothes, *Diplomarbeit*, TU Chemnitz **2008**. [4] J. Kühnert, T. Rüffer, P. Ecorchard, B. Bräuer, Y. Lan, A.K. Powell, H. Lang, *Dalton Transactions* **2009**, 4499. [5] A. Abylaikhan, *Dissertation*, TU Chemnitz **2005**. [6] L.K. Singh, S. Mitra, *Thermochim. Acta*, 138, **1989**, 285. [7] P. Chaudhuri *et al.*, *J. Chem. Soc. Dalton Trans*., **1988**, 1367.

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