SP2. Synthesis of Multimetallic High-Spin Complexes

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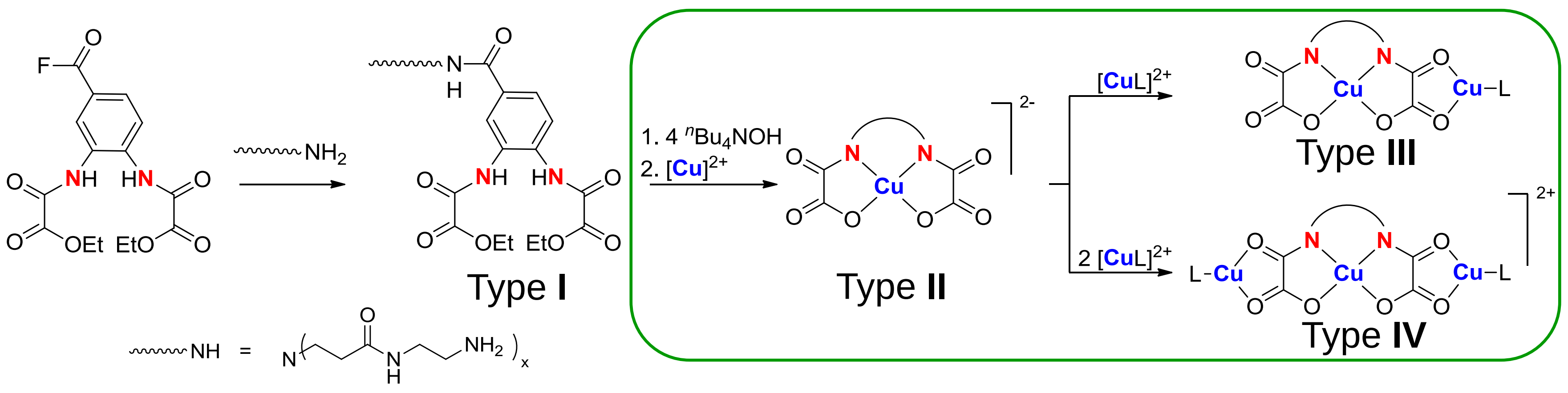
Introduction

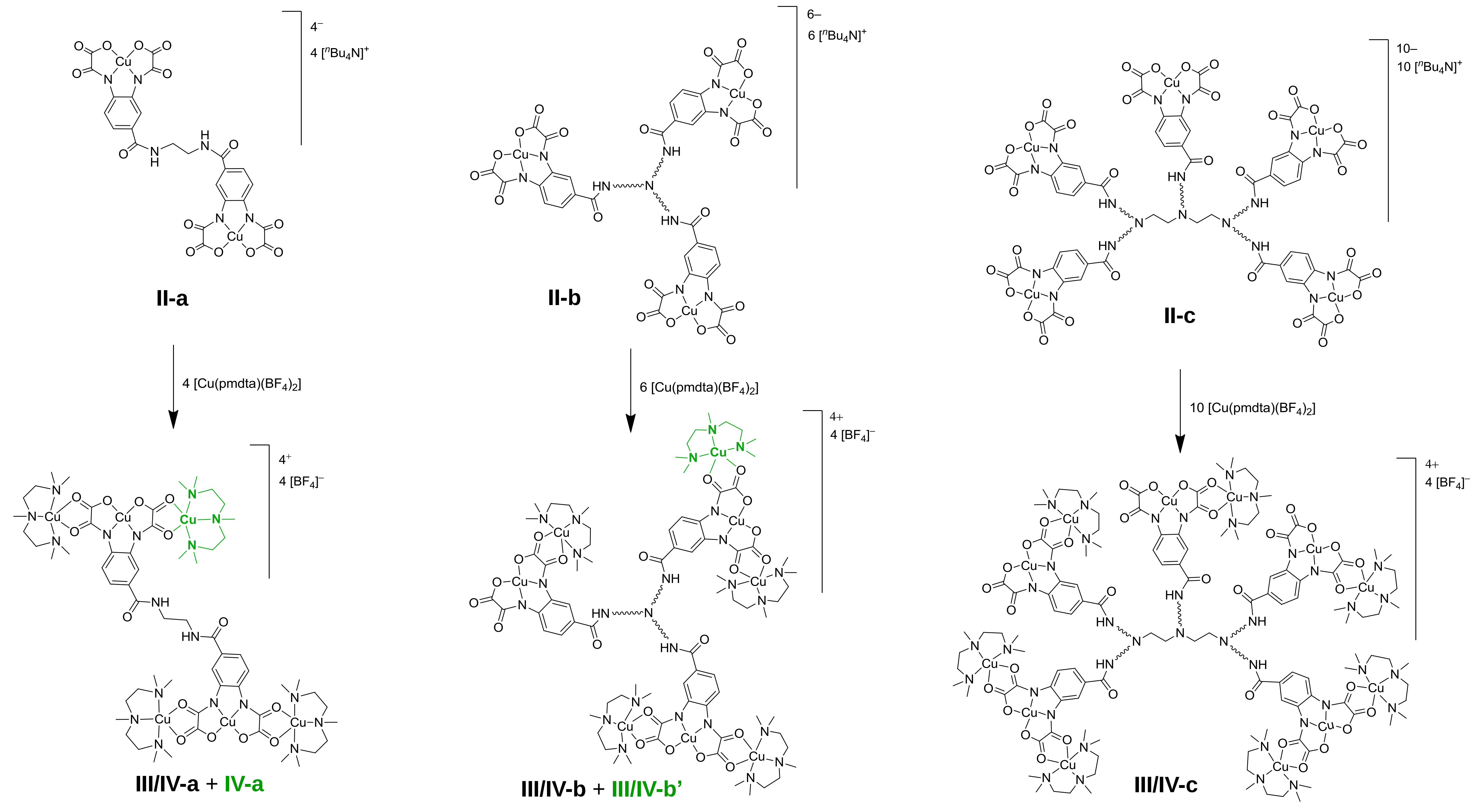
A high number of trimetallic copper(II) oxamato-bridged complexes (Scheme 1) have already been synthesized and characterized and magnetic measurements have also been carried out. For five-coordinated terminal copper(II) ions (type **III** and **IV**, L e.g. pmdta) of trinuclear bis(oxamato) type complexes 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 copper(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** molecule and type **II – IV** complexes (L = pmdta; N,N,N',N",N"-pentamethyldiethylentriamine)*

Preliminary Results

The preparation of the type **I** and **II** compounds is shown in Scheme 1. Whereby the precursor molecule for type **I** containing the acyl fluoride substituent, is formed in good quantities out of the carboxylic acid by the reaction of HF-pyridine and *N*,*N'*-Dicyclohexylcarbodiimide [2].
Previous to metalation reactions type **I** molecules have been linked by ethylendiamine (**I-a**) and „dendritic" systems (**I-b** and **c**).
For the linkage PAMAM based dendritic systems have been used containing three (**I-b**) and five (**I-c**) amines as endgroups.
The synthesis of the type **II** compounds (**II-a** – **c**) results out of the reaction of the type **I** molecules with a metal salt (e.g. $CuCl_2(H_2O)_2$) after deprotonation and alkaline hydrolysis (^{n}Bu$_4$NOH) (Scheme 2) [3].
The formation of the type **III** and **IV** complexes results by the reaction with a metal complex e.g. [Cu(pmdta)(BF$_4$)$_2$] depending on the used ratio (Scheme 1).
Reactions to type **II** and **III**/**IV** complexes with dendritic systems containing ten endgroups have been carried out but are not mentioned here due to missing characterization until now.
The products have been characterized by ESI-MS measurements (see Fig. 1 – 3). For all complexes the measured ESI-MS (Electrospray Ionization Mass spectrometry) spectra fit well to the calculated ones.



Scheme 2. *Reaction of type **II** complexes with [Cu(pmdta)(BF$_4$)$_2$] to type **III** and **IV** complexes (the green marked part shows the different with ESI-MS detected complexes).*

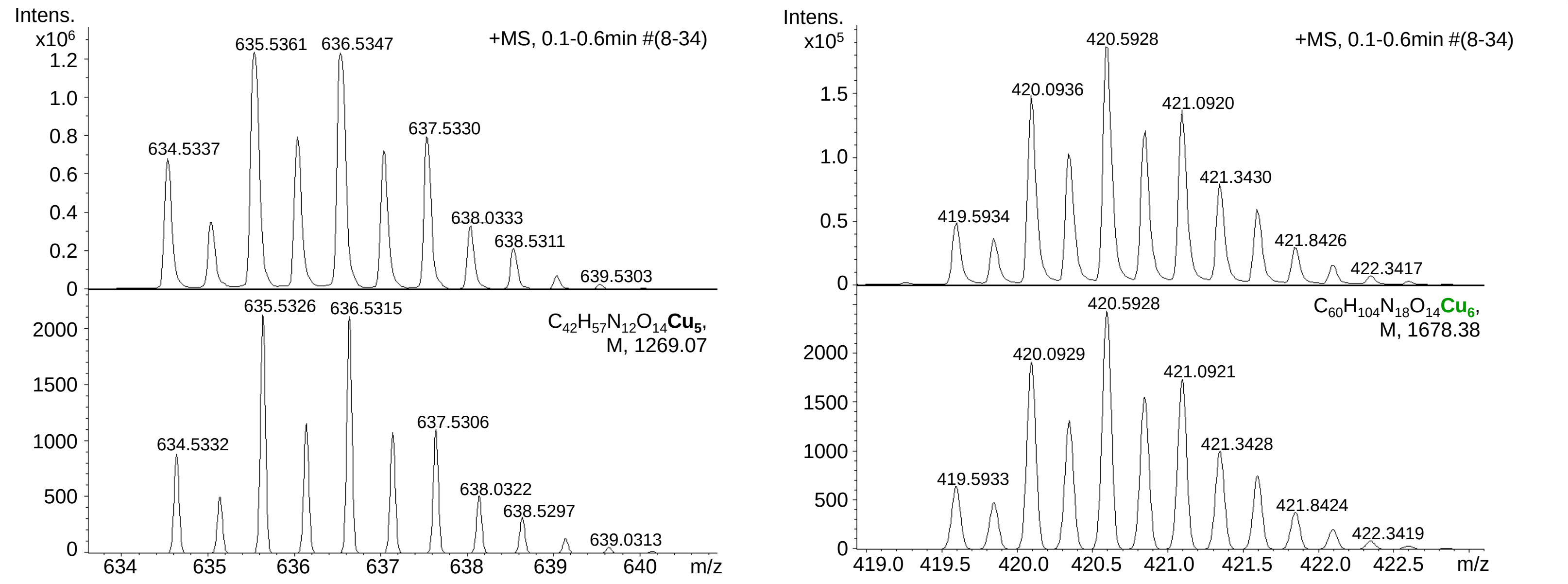


Fig. 1. *ESI-MS spectra of **III/IV-a** and **IV-a** containing five and six Cu(II) ions respectively (upper part: measured spectra, lower part: calculated spectra), whereby the complex type **III/IV** signify a mixture of the explained type **III** and **IV** complexes.*

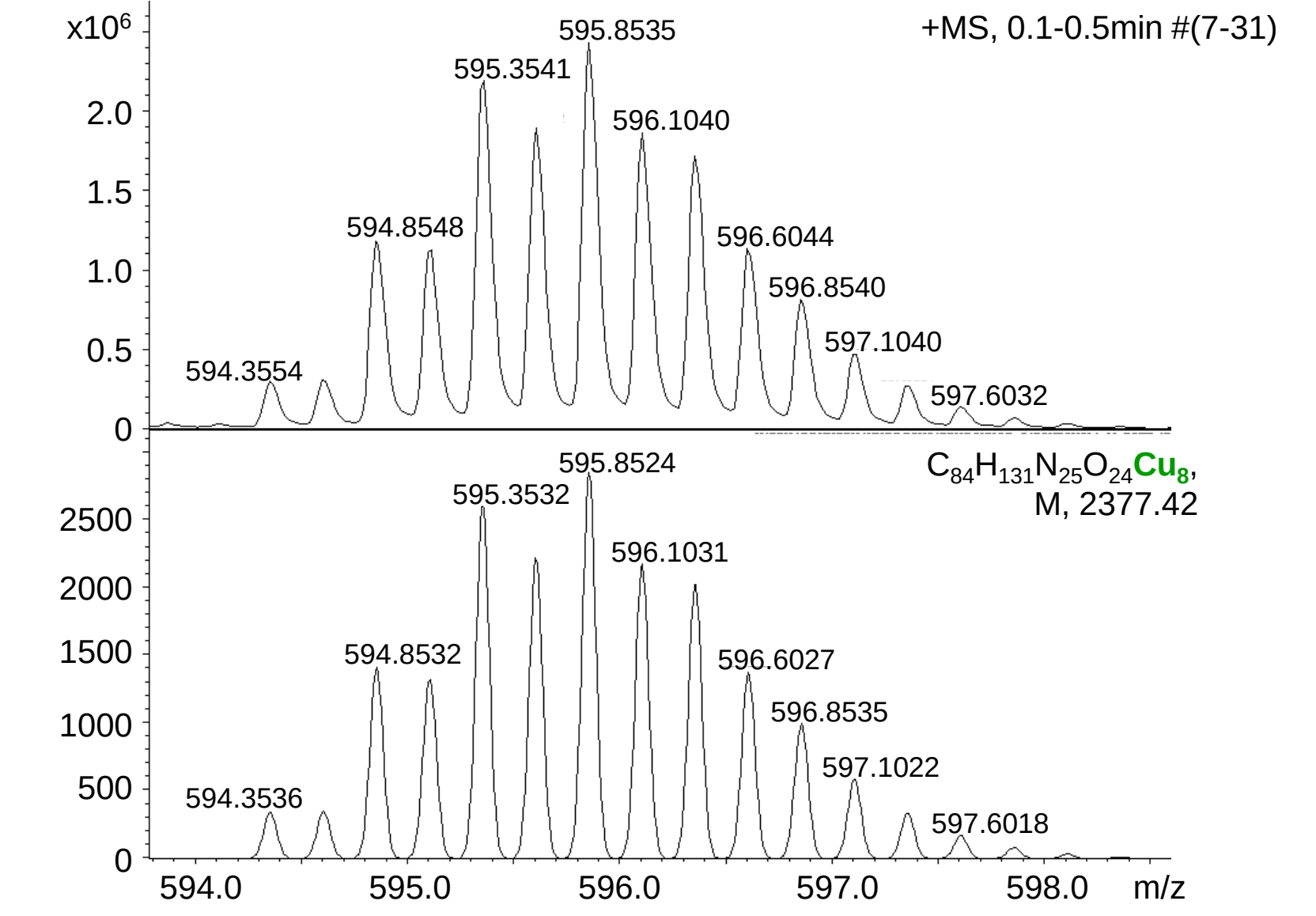


Fig. 2. *ESI-MS spectra of **III/IV-b'** containing eight Cu(II) ions. Further peaks could be found showing the existence of molecules within seven Cu(II) ions (**III/IV-b**).*

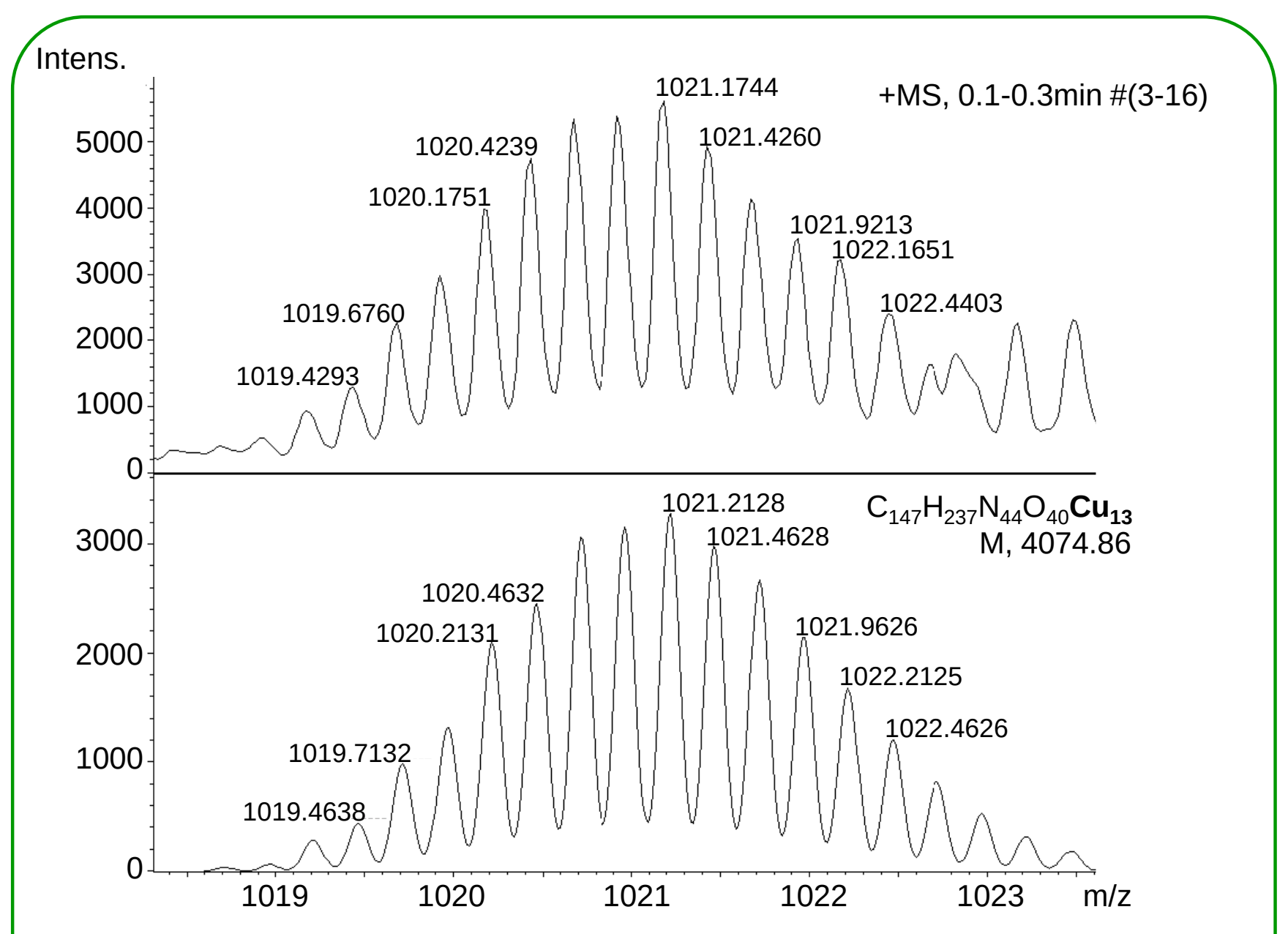


Fig. 3. *ESI-MS spectra of **III/IV-c**, containing 13 Cu(II) ions. Another peak could be found within 12 Cu(II) ions. The spectra of the precursor **II-c** has not been measured until now.*

ESI-MS-Spectra
ESI-MS spectra could be observed of the shown type **III/IV** and **IV** complexes (Fig. 1 – 3). After reaction of the dinuclear Cu(II) complex **II-a** with [Cu(pmdta)(BF$_4$)$_2$] type **III/IV** and **IV** complexes were formed which has been proofed by ESI-MS measurements. The occurrence of a type **III/IV** complex may indicate that a complete metalation of terminal sides is not achieved. Furthermore it cannot be sure, that due to the method of ESI-MS fragmentation did occur.
After the reaction of the higher type **II** complexes **II-b** and **II-c** 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 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 unpaired electrons (**III/IV-c**).
There are two reasons for the absence of peaks from type **IV** complexes of the higher dendritic systems (**b** and **c**) within ESI-MS-spectra: The ionization method fragmentizes the molecules prior it can be detect or the reaction from type **II** to **IV** takes part incomplete. Due to this further characterization has to be done (MALDI-MS).

Outlook

The two nickel(II) complexes shown in Fig. 4 have been invested in our working group [4, 5]. For both complexes a crystal structure could be obtained. The ferrocene containing molecule shows also a ferromagnetic coupling between the Ni(II) ions (Fig. 5). Due to the structural conformities of these two complexes a similar magnetic behavior of the Ni(II)-formate complex could be assumed which has to be proofed.
Furthermore the presence of the two ferrocene substituents motivates us to study the spectro-electro chemistry and to investigate the impact to the magnetical properties after oxidizing Fe(II) to Fe(III).

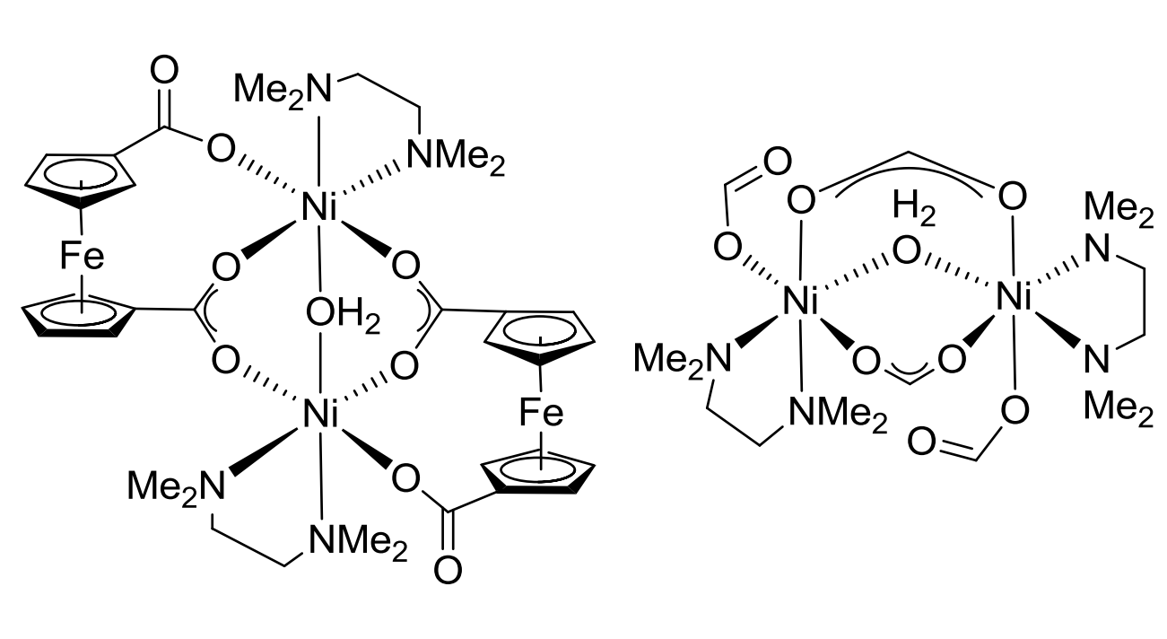


Fig. 4. *Ni(II)-dimers both bridged by two carboxylates and one water ligand* [4, 5].

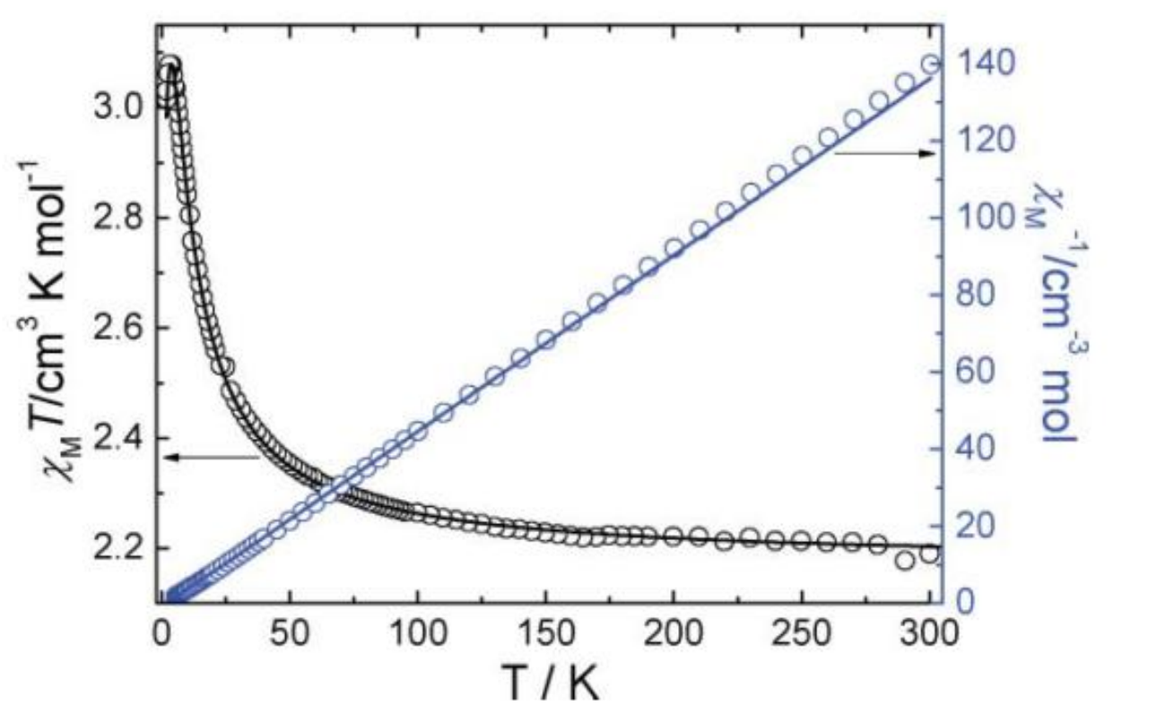


Fig. 5. *Plot of χ_M^{-1} and $\chi_M T$ vs. T for ferrocene containing dimer. Circles: experimental values, solid line: theoretical curve* [4].

References & Acknowledgement

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