

Quantitative determination of iron in spin transition complexes with dendritic ligands

C. M. Grunert¹, K. Eberhardt², P. Gütlich¹, P. Thörlé²

¹ Institut für Anorganische Chemie und Analytische Chemie and ² Institut für Kernchemie, Universität Mainz, D-55099 Mainz, Germany;

Transition metal complexes with spin crossover (sco) behaviour have been studied since the last seven decades, in fundamental research and, during the last decade, towards the objective of potential industrial applications [1]. Particular effort has been invested in tuning the material properties to optimize their spin transition behaviour. Among others, liquid crystalline sco materials [2] and sco complexes with dendritic ligands [3] have been published recently.

In the case of Fe^{II} complexes with dendritic ligands the mass ratio of Fe^{II} (55.8 g/mol) to the organic ligands ^a (between ca. 1500 and 3000 g/mol) is very low and elemental analysis (C,H,N) is not sufficient to determine the metal to ligand ratio satisfactorily. Atom absorption spectroscopy for the quantitative determination of the Fe^{II} content fails because of the low solubility of the complexes in water and the high stability of the dendritic ligands to acids and bases. Methods like X-ray fluorescence spectroscopy would not give quantitative information with the desired precision. However, the exact knowledge of the iron content and the molecular mass of the complex is required for the correct determination of the molecular magnetic susceptibility, which represents the most important characterisation of these materials and which is obtained by magnetic measurements.

Neutron activation analysis (NAA) may be carried out on liquid solutions or solid material. The samples of the dendronised complexes and iron(II) sulphate as reference were irradiated for 6 h with thermal neutrons in the TRIGA Mark II research reactor of the Institut für Kernchemie at a flux of $7 \times 10^{11} \text{ n}/(\text{cm}^2\text{s})$ affording the nuclear reaction $^{58}\text{Fe}(n,\gamma)^{59}\text{Fe}$. After a delay of about two weeks for allowing short-lived radioactive nuclides to decay, the activity of ^{59}Fe with a half-life of 44.5 d could be determined by γ -spectrometry (192 keV, 1099 keV and 1293 keV), generated by β^- decay of ^{59}Fe to ^{59}Co . The iron content is given by the ratio of the activities of the sample compared to the reference.

The results of the quantitative Fe determination of sco complexes with the type $[\text{Fe}(\text{G}_n\text{-PBE})_3]_A \cdot x\text{H}_2\text{O}$ (PBE = poly benzyl ether with $n = 1, 2$ and $A = \text{triflate, tosylate}$) are presented.

^a Thanks are due to Prashant Sonar and Dieter Schlüter from ETH-Zürich for providing the project with dendritic ligands

Figure 1 depicts the count rates obtained for the three different γ -ray energies for FeSO₄ as reference material and the dendritic complexes. The plots in figure 1 serve as calibration relationships for the quantitative determination of the iron content in the dendritic spin transition complexes under study. The accuracy of the method is ca. 3 % and is mainly given by the error of the weight of the sample.

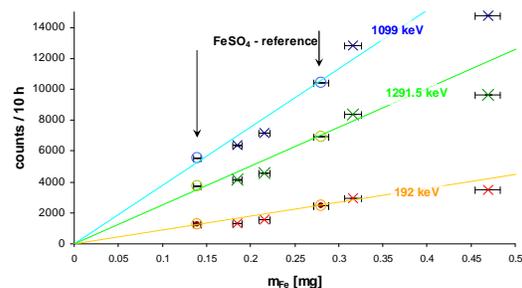


Figure 1: Calibration plots for the quantitative determination of iron in dendritic spin transition materials.

With the Fe-content and the quantitative determination of solvent molecules by thermogravimetric analysis, it is possible to calculate the molecular weight of the complex and to determine the correct amount of ligands. The results from C,H,N-analysis can be taken to check the results.

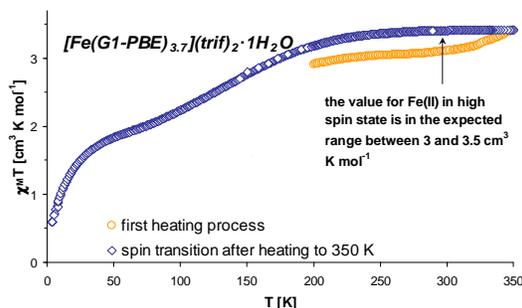


Figure 2: The results of NAA enable for a calibration of magnetic measurements.

References

- [1] P. Gütlich, H.A. Goodwin (eds.), Top. Curr. Chem.; **233-235**; Springer Berlin-Heidelberg-New York, 2004.
- [2] Y. Galyametdinov *et al.*, Angew. Chem. Int. Ed. **40**, 4269, (2001).
- [3] T. Fujigaya *et al.*, JACS, **127**, 5484, (2005).