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Mössbauer Spectroscopic Study and Magnetic Investigation of Iron(III) Complexes on a Dendrimeric Basis

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Abstract. The functionalization of the molecular surface of various dendrimer generations with a phosphorous core and external amine groups is obtained by converting those amine groups into the corresponding imines of salicylaldehyde creating multiple coordination sites for the iron atoms. Treatment with iron(III) chloride yields multinuclear iron(III) complexes on a dendrimeric basis. The obtained multinuclear molecular systems exhibit extremely high total spin values. The influence of the generation growth on this type of coordination compounds is investigated by Mössbauer spectroscopy and SQUID magnetometry.

1. Introduction

One current topic in the research field of polymers are dendrimers [1]. These macromolecules have a tunable hyperbranched as well as defined structures and are built generation after generation by repetition of a series of reactions, starting from a central core [2]. Furthermore, a monodisperse nature and high end-group functionality are features of dendrimers. As consequence of these properties, it is possible to get several transition metals into one molecule by creating coordination sites at the end-groups [3, 4]. The dendrimeric backbone has the advantage that every further generation increases the number of metal atoms that can be bound in one molecule. The idea behind synthesizing dendrimers with higher generation numbers and many transition metals, respectively, is the systematic tuning of the magnetic properties in any generation [5]. In this way, a large number of complexes can be obtained on small area – a method, which could achieve high densities in possible applications: optoelectronics, catalysis, biology and photophysical processes.

In this contribution, various dendrimer generations with phosphorous core and external amine groups are functionalized to yield iron(III) complexes bridged via a dendrimeric backbone. The products are studied by Mössbauer spectroscopy and SQUID magnetometry [6-8].



2. Experimental Section

Syntheses of the dendrimeric backbone have been carried out by adapting the description in reference [1, 2].

2.1. First generation dendrimeric nitrile

The amine P_0 (3.4 mmol) was dissolved in distilled water and acrylonitrile (122.75 mmol) was added dropwise. After stirring at 80 °C for 12 h the resulting yellow solution was evaporated to dryness. Yield: 83 % ($M = 523.67$ g/mol).

IR (KBr): ν (cm^{-1}) = 3358 cm^{-1} (N-R, val.), 2934 cm^{-1} (CH_2 , val.), 2250 cm^{-1} ($\text{C}\equiv\text{N}$, val.).

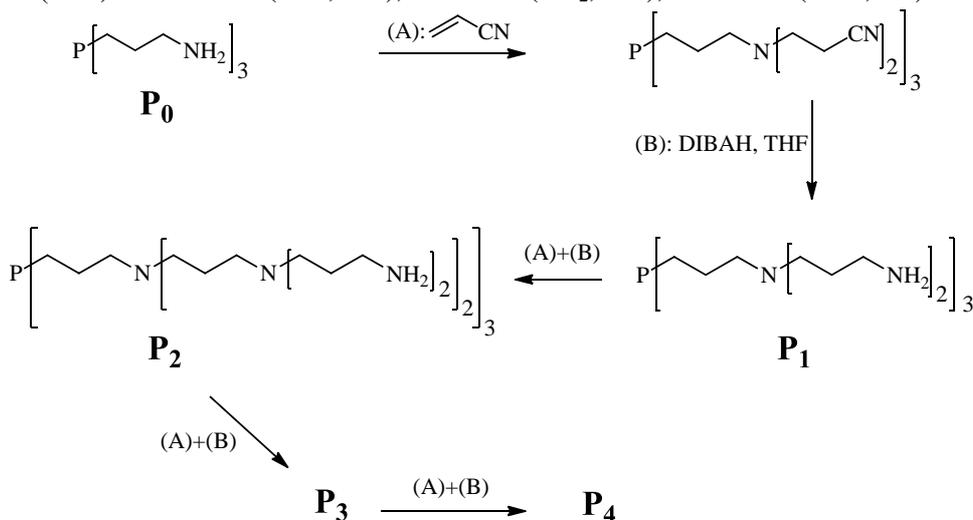


Figure 1. Step by step synthesis of a dendrimer with terminal amines from zeroth to fourth generation

2.2. First generation dendrimeric amine P_1

To a solution of the nitrile P_1 (1.68 mmol) in dry THF (300 ml) a 1M solution of DIBAH in heptane (28.22 mmol) was added dropwise under nitrogen atmosphere. The mixture was heated to 80 °C for 48 h. After adding methanol (400 ml) the precipitated aluminium salt was filtered off and the resulting yellow solution was evaporated to dryness. Yield: 86 % ($M = 574.86$ g/mol).

IR (KBr): ν (cm^{-1}) = 3354 cm^{-1} (N-R, val.), 2934 cm^{-1} (CH_2 , val.), 1664 cm^{-1} (NH_2 , val.).

2.3. Higher generation dendrimeric nitriles and amines

The dendrimeric nitriles and dendrimeric amines of the second (P_2), third (P_3) and fourth (P_4) generation, respectively, were synthesized in analogy to the first generation (P_1) starting from the respective previous generation. (See Fig. 1)

Table 1. Reaction parameters for the synthesis of the corresponding nitriles.

	Educt [mmol]	Acrylonitrile [mmol]	Yield [%]	$\nu(\text{C}\equiv\text{N})$ [cm^{-1}]
nitrile P_2	1.73	125	60	2248
nitrile P_3	1.2	172	69	2247.3
nitrile P_4	0.33	95	96	2246.8

Table 2. Reaction parameters for the synthesis of the corresponding amines.

	Educt [mmol]	DIBAH [mmol]	Yield [%]	$\nu(\text{NH}_2)$ [cm^{-1}]
amine P₂	0.50	16	75	1660.3
amine P₃	0.35	23	81	1650.6
amine P₄	0.23	31	63	1655

2.4. Functionalization and complexation of dendrimers

Syntheses of the coordination compounds on the dendrimeric surface have been carried out by adapting the description in [3, 4].

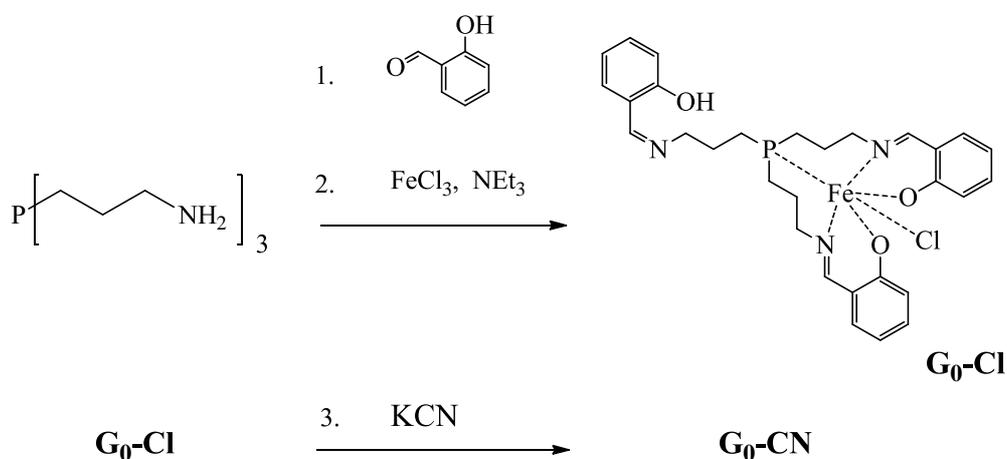


Figure 2. Synthesis of an iron(III) dendrimer compound, starting from a zeroth generation dendrimer and subsequent monodentate ligand-exchange with potassium cyanide.

The corresponding amine P₀ (3.16 mmol) was dissolved in methanol. The mixture was heated under reflux for 10 min and salicylaldehyde (10.42 mmol) was added dropwise. After 30 min of stirring at room temperature a solution of anhydrous iron(III) chloride (3.16 mmol) was added slowly. The resulting solution was heated to 50 °C for 5 min and triethylamine (6.32 mmol) was added. Reducing the solvent and subsequent cooling precipitated the product. A solid G₀-Cl was collected and dried under reduced pressure. Yields: 60 %, (M= 606.89 g/mol).

IR (KBr): ν (cm^{-1}) = 3418 cm^{-1} (N-R, val.), 2925 cm^{-1} (CH₂, val.), 1612 cm^{-1} (C=N, val.).

The synthesis of the dendrimeric compounds of the first, second, third and fourth generations were performed in analogy to the zeroth generation (see Fig. 2, step 1&2 and Table 3) starting from the respective dendrimer generation P₁, P₂, P₃ and P₄.

Table 3. Reaction parameters for the synthesis of the corresponding complexes G_n-Cl (n: generation number).

	Salicyl. [mmol]	FeCl ₃ [mmol]	NEt ₃ [mmol]	Yield [%]
G₁-Cl	9.91	4.19	8.38	61
G₂-Cl	5.88	4	4.8	58
G₃-Cl	6.91	2.5	5	50
G₄-Cl	6.28	2.5	5	45

2.5. Ligand exchange with cyanide

The sixth coordination site, a chloride ion, was exchanged by a cyanide ion via reaction with potassium cyanide (see Fig. 2, step 3): The dendrimeric complex $G_0\text{-Cl}$ was dissolved in methanol and stirred for 4 h at 50 °C. Then, KCN as powder was added carefully in the reagent flask and the solution was stirred 1 h at room temperature. Reducing the solvent and subsequent cooling precipitated the product. The product $G_0\text{-CN}$ was collected and dried under reduced pressure.

Yield: 75%, ($M = 597.94$ g/mol).

IR (KBr): ν (cm^{-1}) = 3407 (N-R, val.), 2044 ($\text{C}\equiv\text{N, val.}$), 1618.7 (C=N, val.).

The procedure for higher generation cyanides was performed in analogy.

Table 4. Reaction parameters for the synthesis of the corresponding complexes $G_n\text{-CN}$.

	KCN [mmol]	Yield [%]		KCN [mmol]	Yield [%]
$G_1\text{-CN}$	1	75	$G_3\text{-CN}$	1	75
$G_2\text{-CN}$	1	79	$G_4\text{-CN}$	1	63

3. Analytical Data for Dendrimer Compounds

All compounds were characterized by IR spectroscopy and ESI-MS. The IR spectra were measured in KBr pellets (Bruker Optics Tensor) in the $4000\text{-}400$ cm^{-1} region at ambient temperatures. ESI mass spectra were recorded by “Finnigan MAT LCQ” in methanol (SupraSolv).

Infrared spectroscopy has proved to be a very useful tool to monitor the dendrimeric build-up of certain hyperbranched structures [9-12]. For the synthesized amines, the IR spectra exhibit a band in the range of $1664\text{-}1650$ cm^{-1} characteristic for NH stretching vibrations. For synthesized nitriles (see Fig. 1), one band appears in the range of $2250\text{-}2246$ cm^{-1} characteristic of $\text{C}\equiv\text{N}$ stretching vibrations, whereas the NH stretching vibrations practically completely disappear. Vice versa, the $\text{C}\equiv\text{N}$ stretching vibration band disappears after the reduction with DIBAL-H and NH band appears again. For synthesized complexes (see Fig. 2) bands in the range $1622\text{-}1611$ cm^{-1} are corresponding to the stretching vibration of C=N of the imine group, which show a significant shift under the influence of generation growth and ligand-exchange. (See Tab. 5).

Selected examples of ESI-MS signals of different dendrimeric compounds are given below in tabular form (see Tab. 5). Due to the hyperbranched structure of the dendrimer compounds molecular peaks have been detected seldom in the ESI-MS despite its gentle ionisation method. Nevertheless, a tendency for a relative increase in the number of fragments with high mass-to-charge (m/z) ratios can be observed for higher generation numbers.

Another method suggesting the successful generation built-up of the compounds is the SQUID magnetometry. Those results will be presented below (see Paragraph 5).

Table 5. Selected examples of infrared spectroscopy bands and electrospray ionisation mass spectrometry (ESI-MS) signals of different dendrimeric complexes.

	M [g/mol]	$\nu(\text{C=N})$ [cm^{-1}]	ESI-MS m/z		M [g/mol]	$\nu(\text{C=N})$ [cm^{-1}]	ESI-MS m/z
$G_0\text{-Cl}$	606.89	1612	304.2 ($z=2$)	$G_0\text{-CN}$	597.94	1618.7	599.4 ($z=1$)
$G_1\text{-Cl}$	1440.36	1617	441.1 ($z=3$)	$G_1\text{-CN}$	1430.92	1620.7	441.8 ($z=3$)
$G_2\text{-Cl}$	3017.99	1617.7	613 ($z=5$)	$G_2\text{-CN}$	2961.38	1621.4	588 ($z=5$)
$G_3\text{-Cl}$	6173.28	1611.5	996 ($z=6$)	$G_3\text{-CN}$	6060.07	1621.8	865.6 ($z=7$)
$G_4\text{-Cl}$	12438.8	1611.3	1234,6 ($z=10$)	$G_4\text{-CN}$	12212.42	1621.5	1745 ($z=7$)

4. Mössbauer Spectroscopy: Results and Discussion

Mössbauer spectra were recorded using a conventional transmission spectrometer at $T = 20$ K and $T = 300$ K. $^{57}\text{Co}/\text{Rh}$ was used as the source of the radiation and the isomeric shift data are given relative to Fe in Rh at room temperature.

Fig. 3 and Table 6 show the Mössbauer spectra and parameter of the dendrimeric complexes from zeroth to fourth generation. Mössbauer spectra of all dendrimeric compounds at 300 K and at 20 K consist of a signal with the shape of a simple line doublet indicative for Fe(III) in the high-spin state ($S=5/2$).

In case of the $G_n\text{-Cl}$ dendrimers, the spectra could be described best by a fit with 2 Lorentzian doublets. Since one would not expect discrete positions for the iron centres, for isomeric shift (IS) values the centre of gravity was determined for the complete signal in order to achieve better comparability within this discussion. Respective mean values for the quadrupole splitting (QS) were determined as well.

At 300 K all spectra show typical values for the IS in the range 0.2440(36)-0.2936(85) mm/s, showing the maximum value for the third generation. A maximum was found at low temperature as well. At 20 K the values of the IS are in the range of 0.3459(40)-0.4066(38) mm/s and are therefore well in accordance with the "Second-Order Doppler Shift".

The QS values exhibit a slight temperature dependence. Values in a range of 0.599(36)-1.132(93) mm/s indicate a deviation from an ideal octahedral coordination sphere. The differences occurring on generation growth could be explained by influences of different conformations and agglomeration degrees on the symmetry of the coordination sphere and therefore the electric field gradient.

Figure 4 displays the mean values for the isomeric shift and the quadrupole splitting for the $G_n\text{-Cl}$ ($n: 1-4$) series for 20 and 300 K - visualizing the "Second-Order Doppler Shift" and the generation effect on the electric field gradient.

In case of the $G_n\text{-CN}$ dendrimers, a strong asymmetry of the Mössbauer doublet is observed. This asymmetry is particularly pronounced for the lower generations and seems to be temperature dependent. In general, an asymmetric absorption signal in the Mössbauer spectroscopy can be caused by a texture, Goldanski-Karyagin or relaxation effects. The temperature dependence as well as the similar areas of the two resonant lines lead to the assumption that this asymmetry is caused by (spin-spin) relaxation.

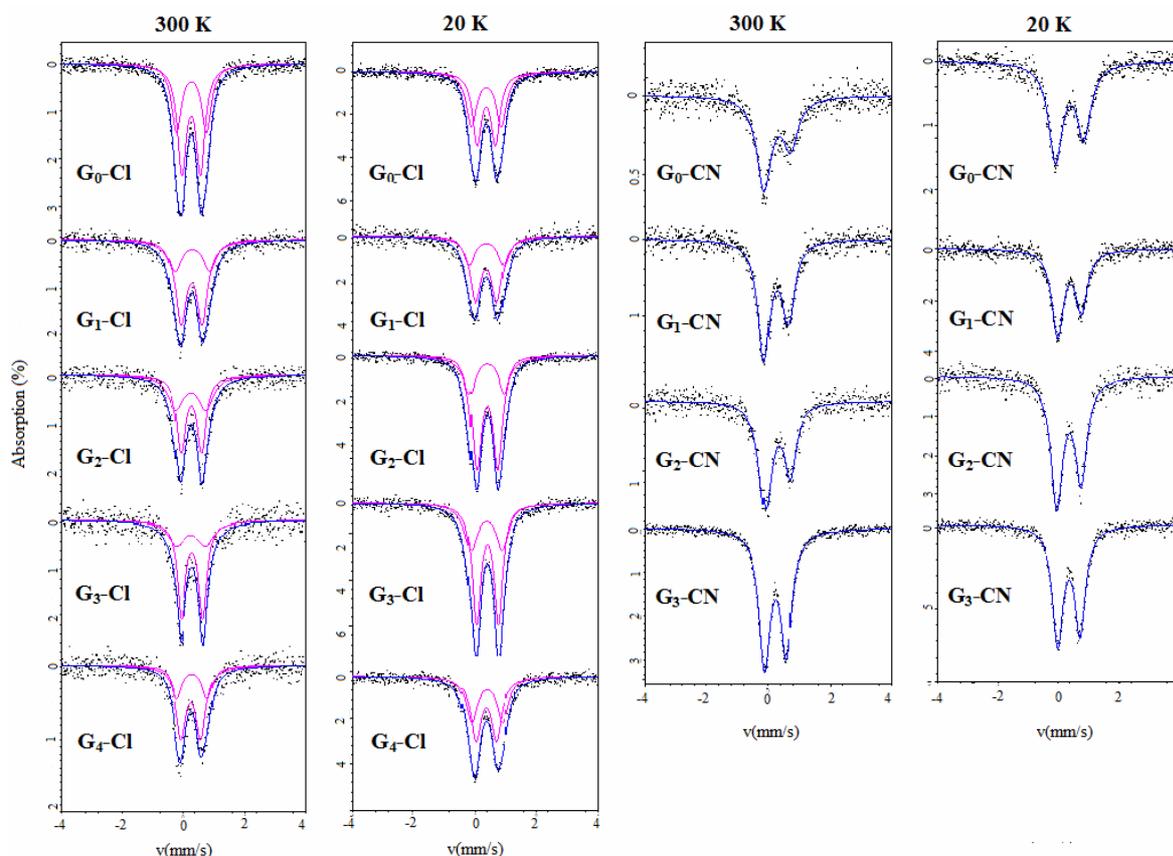


Figure 3. Mössbauer spectra at 300 K and at 20 K of Iron(III) dendrimer compound from zeroth to fourth generation.

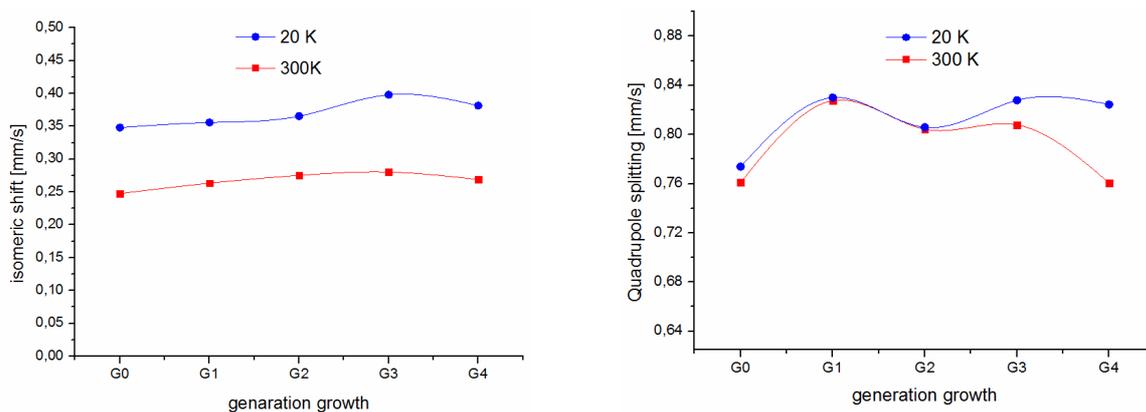


Figure 4. Dendrimeric complexes G_n -Cl (n : 1-4): temperature-dependence of the mean isomeric shift (left), and the mean quadrupole splitting (right).

5. Magnetometry: Results and Discussions

Magnetic susceptibility and magnetisation measurements were performed using a SQUID magnetometer (Quantum Design MPMS-XL) within a temperature range of $T = 2 - 300$ K and an applied external magnetic field of $B = 0.1$ T. Field-dependent magnetization data were taken at $T = 5$ K. The effective magnetic moment has been calculated using $\mu_{\text{eff}} / \mu_B = 798 (\chi T)^{1/2}$ when SI units are employed. The results were corrected for the magnetisation of the sample holder and for the diamagnetic contributions, which were estimated from Pascal constants.

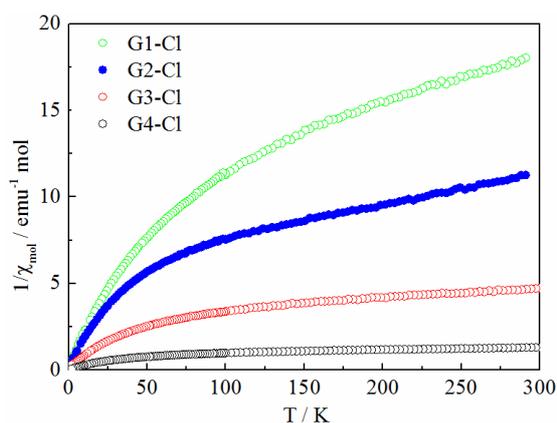


Figure 5. Temperature dependence of a plot of inverse susceptibility for dendrimeric complexes $G_n\text{-Cl}$ (n : generations number) in different generations.

All $\chi^{-1}(T)$ curves (see Fig. 5) deviate strongly from a linear behaviour and only at higher temperatures the susceptibilities were found to follow the Curie-Weiss relationship.

By extrapolation to the x-axis negative values of Weiss constant θ were found which indicate an antiferromagnetic behavior of the compounds. For all four dendrimer generations this antiferromagnetism appears to be temperature dependent: It decreases with temperature reduction and increases with a temperature rise. The increase due to heating can be explained by the occupation of thermally populated states or by cooperative effects underlying the model of superexchange. It is apparent that the critical temperature above which linear Curie-Weiss behavior occurs strongly depends on the dendrimer generation number. Furthermore, it can be observed that the smaller the generation number is the more negative appears the extrapolated Weiss constant, thus, indicating a weaker antiferromagnetic coupling between the spin-bearing iron centres for higher generation numbers which is probably due to inferior magnetic exchange paths within the large molecules.

The temperature dependence of the effective magnetic moment μ_{eff} seems not to have reached saturation at room temperature, whereas the slope of the curve varies heavily with the generation number (see Fig. 6, left). This observation suggests significantly higher values of the total spin for higher generation numbers.

The field-dependent magnetization M exhibits a similar tendency (Fig. 6, right): Saturation of the sample seems to be reached at lower external field-strengths for lower generation numbers.

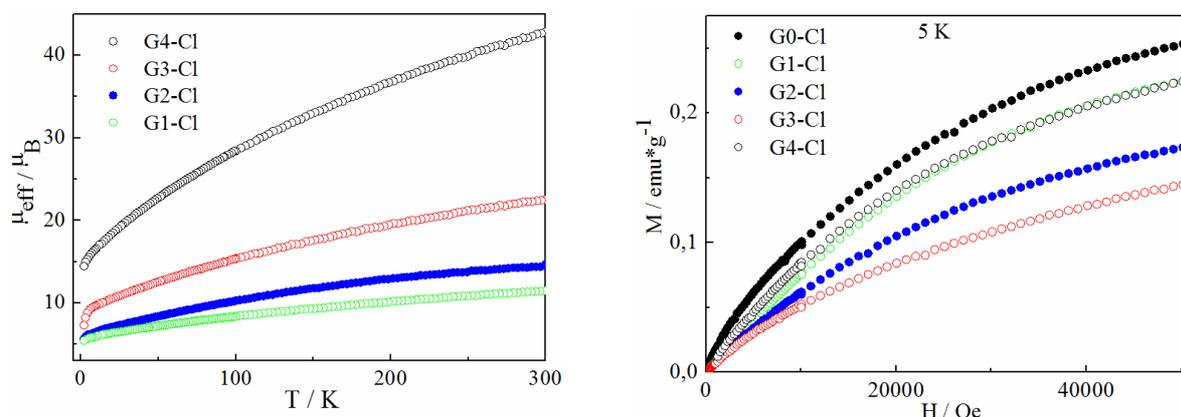


Figure 6. Temperature dependence of effective magnetic moment (left) and field dependence of the magnetization at 5 K (right) for dendrimeric complexes $G_n\text{-Cl}$ in different generations.

6. Conclusions

In this contribution, multinuclear iron(III) compounds with a dendrimeric backbone were synthesized and characterized via IR spectroscopy, Mössbauer spectroscopy and SQUID magnetometry.

Even though a pantadente ligand providing a N_3O_2 coordination surrounding for the iron(III) was chosen which enabled spin crossover in previous studies [4, 6-7], a spin transition could not be detected. Rather, Mössbauer spectroscopic measurements indicate all iron(III) centres to be in their high spin state in the temperature range investigated (20-300 K). The isomeric shifts are slightly influenced by the generation growth whereas quadrupole splittings were found to be strongly dependent on the generation number. A ligand exchange in the position of the monodentate ligand from chloride to cyanide led to a strong asymmetry of the Mössbauer doublet. This asymmetry is particularly pronounced for the lower generations and can probably be explained by relaxation processes or texture effects.

The magnetic investigations revealed antiferromagnetically coupled molecular systems with higher magnetic moments for higher generation numbers. Even the cooperative interactions of the spin bearing centres exhibit a remarkable generation effect: The antiferromagnetic interaction decreases with an increasing generation number which is probably due to inferior magnetic exchange paths.

All results outline the possibility to create molecular systems with extremely high total spin values using the dendrimeric approach.

Table 6. Mössbauer parameters of dendrimer compounds in different generations: Before and after a monodentate ligand exchange.

Compound	T(K)	Fe(III) HS-state			Fe(III) HS-state		
		δ [mm/s]	Δ [mm/s]	Fraction [%]	δ [mm/s]	Δ [mm/s]	Fraction [%]
G₀-Cl	300	0.2440(36)	0.608(30)	59	0.2529(57)	0.980(55)	41
	20	0.3459(40)	0.599(36)	53	0.3508(53)	0.970(59)	47
G₀-CN	300	0.278(16)	0.860(28)	100	---	---	---
	20	0.3636(86)	0.932(15)	100	---	---	---
G₁-Cl	300	0.2545(64)	0.690(40)	69	0.280(18)	1.132(93)	31
	20	0.364(16)	1.119(74)	32.6	0.355(15)	0.690(11)	67.4
G₁-CN	300	0.2496(78)	0.7591(14)	100	---	---	---
	20	0.3528(70)	0.781(13)	100	---	---	---
G₂-Cl	300	0.283(12)	0.672(61)	57	0.265(34)	0.98(47)	43
	20	0.3653(24)	0.6772(19)	69.1	0.3657(72)	1.093(69)	30.9
G₂-CN	300	0.2769(90)	0.793(16)	100	---	---	---
	20	0.3672(63)	0.800(11)	100	---	---	---
G₃-Cl	300	0.2936(85)	0.720(30)	66	0.254(60)	0.977(65)	34
	20	0.4066(38)	0.7142(18)	63	0.383(12)	1.021(13)	37
G₃-CN	300	0.2557(22)	0.7148(38)	100	---	---	---
	20	0.3658(34)	0.7364(60)	100	---	---	---
G₄-Cl	300	0.258(11)	0.650(35)	68	0.292(23)	0.994(68)	32
	20	0.3676(55)	0.677(18)	56.2	0.3990(78)	1.013(18)	43.8

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