Iron(III) Complexes on a Dendrimeric Basis and Various Amine Core Investigated by Mössbauer Spectroscopy

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Iron(III) Complexes on a Dendrimeric Basis and Various Amine Core Investigated by Mössbauer Spectroscopy

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Abstract. Dendrimers of various generations were synthesized by the divergent method. Starting from various amine cores (G_{0a}, G_{0b}, G_{0c}) the generations were built by reaction of the amine with acrylnitrile followed by hydrogenation with DIBAL-H. Treatment with salicylaldehyde creates a fivefold coordination sphere for iron in the molecular periphery. The resulting multinuclear coordination compounds are investigated by Mössbauer spectroscopy.

1. Introduction

Dendrimers represent a novel type of polymeric materials that have been of increasing interest in recent years revealing applications in supramolecular chemistry, nanoscience, medicine and catalysis [1]. These macromolecules are defined as highly branched, spherical and monodisperse molecules composed of monomers that spread from a central core [2]. The dendrimers are produced in iterative sequences of reactions steps, whereby any further sequence leads to a higher generation dendrimer. (See Fig. 1)

In this study, we focused on divergent approach, where the molecule grows from the core to the periphery and whereas convergent synthesis first builds up the dendrons called arms, wich were connected in a merging step to the core fragment. The extraordinary topology of the dendrimers was used to yield multinuclear iron(III) complexes by functionalizing the terminal amine groups and subsequently to observe the influence of the generation growth on the spin state of the resulting metal complex with Mössbauer spectroscopy [3-7].

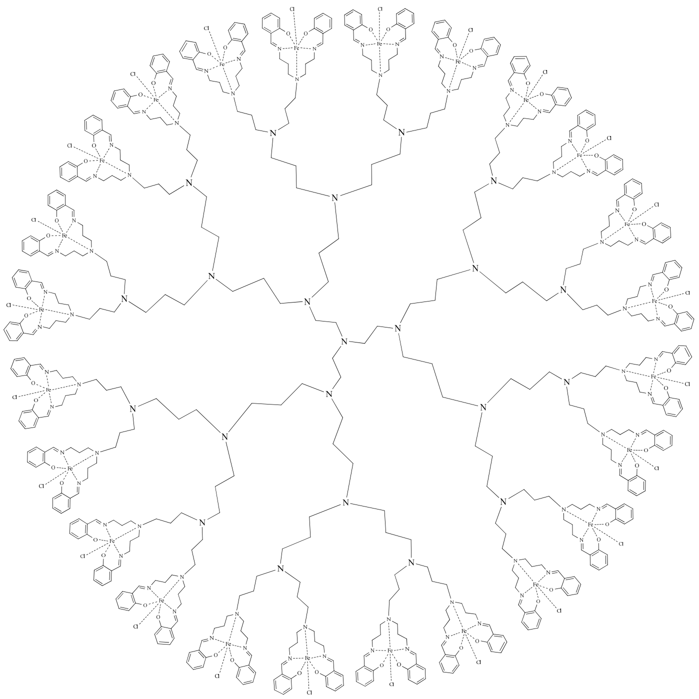


Figure 1. Scheme of a fourth generation dendrimer complex G_{4a}.

2. Experimental Section

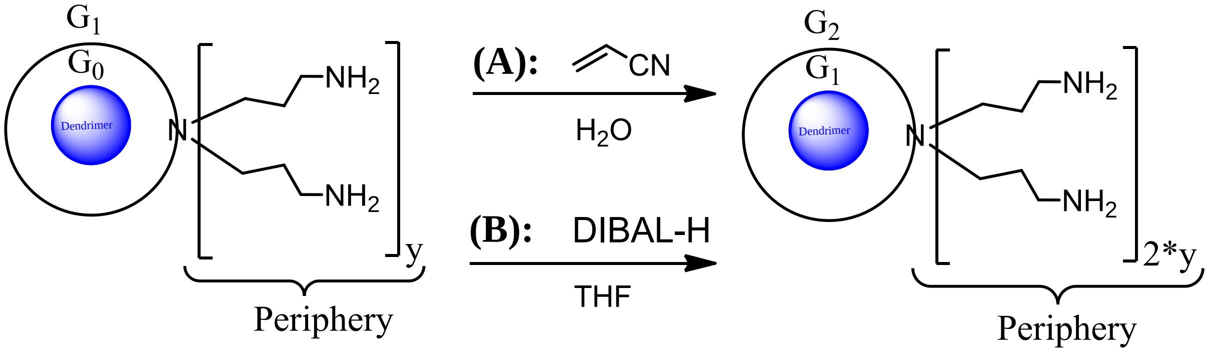
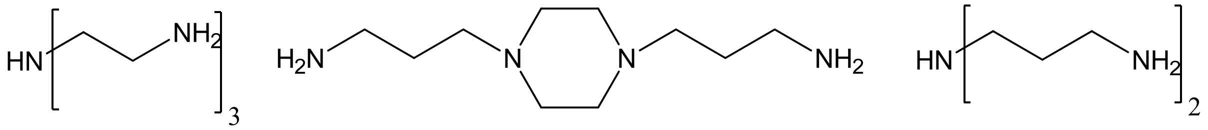


Figure 2. Generation growth of dendrimeric amine; y: indicates number of amines at the molecular periphery.



G_{0a} G_{0b} G_{0c}

Figure 3. Scheme of the different amine cores. The subscript numbers indicate the generation; the subscript letters indicate the respective core.

2.1. First generation dendrimeric nitrile G_{1a}

The amine G_{0a}(3 mmol) wasdissolved in distilled water and acrylnitrile (108 mmol) was added dropwise. After stirring at 80 °C for 12 h the resulting yellow solution was evaporated to dryness. Yield: 87 %, (M= 464.31 g/mol).
IR (KBr): ν(cm^{-1}) = 3350 cm^{-1}(N-R, val.), 2954 cm^{-1} (CH_2, val.), 2247cm^{-1} (C≡N, val.).

2.2. First generation dendrimeric amine G_{1a}

To a solution of the nitrile G_{1a} (2 mmol) in dry THF a 1M solution of DIBAL-H in heptane (33.6 mmol) was added dropwise under nitrogen atmosphere. The mixture was heated to 80 °C for 48 h. After adding methanol the precipated aluminium salt was filtered off and the resulting yellow solution was evaporated to dryness. Yield: 81%, (M= 484.47 g/mol).
IR (KBr): ν (cm^{-1}) = 3341cm^{-1}(N-R, val.), 2926 cm^{-1} (CH_2, val.), 1643 cm^{-1} (NH_2, val.).

2.3. Higher generation dendrimeric nitrile and amine

The dendrimeric nitriles and dendrimeric amines of the second (G_2), third (G_3) and fourth (G_4) generation were synthesized in analogy to first generation dendrimeric nitriles and amines starting from the respective amines and niriles of the previous generation. (See Fig. 2)

Table 1. Reaction parameters for the synthesis of the corresponding amines of dendrimers a, b and c.

	Educt[mmol]	DIBAL-H[mmol]	Yield[%]
amine G_{1a}	0.86	12.38	81
amine G_{2a}	0.44	11.73	95
amine G_{3a}	0.16	8.63	91

	Educt [mmol]	DIBAL-H[mmol]	Yield[%]
amine G_{1b}	1.30	13.2	87
amine G_{2b}	0.43	10.5	72
amine G_{3b}	0.25	12.0	60
amine G_{4b}	0.01	9.46	97

	Educt [mmol]	DIBAL-H[mmol]	Yield [%]
amine G_{1c}	1.46	12.85	91
amine G_{2c}	0.74	13.02	57
amine G_{3c}	0.37	13.18	86
amine G_{4c}	0.18	13.73	87

2.4. Functionalization and complexation of dendrimers

The amine G_{0a} (2 mmol) was dissolved in methanol. The mixture was heated under reflux for 10 min and salicylaldehyde (6.6 mmol) was added dropwise. After 30 min of stirring at room temperature a solution of anhydrous iron(III) chloride (2 mmol) in methaol was added slowly. The resulting solution was heated to 50 °C for 5 min and triethylamine (4 mmol) was added. Reducing the solvent and cooling precipitates the product. A solid G_{0a}-Cl was collected and dried under reduced pressure. Yield: 55 %, (M= 546.87 g/mol).
IR (KBr): ν (cm^{-1}) = 3347 cm^{-1} (N-R, val.), 2935 cm^{-1} (CH_2, val.), 1619 cm^{-1} (C=N, val.).

The synthesis of the dendrimeric compounds of the first (G_1), second (G_2), third (G_3) and fourth (G_4) generations were performed in analogy to the zeroth generation. The synthesis of dendremeric compounds with a different coreG_b and G_c were performed in analogy to G_a. (See Fig. 3 & 4)

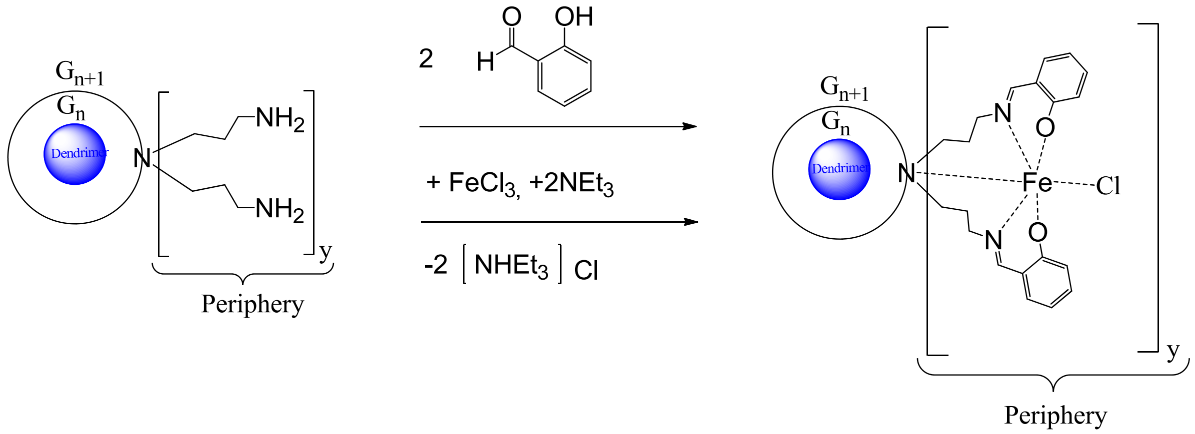


Figure 4. Scheme of the functionalization and the complexation of dendrimers; n: generation number.

Table 2. Reaction parameters for the synthesis of the corresponding complexes G$_{na}$-Cl, G$_{nb}$-Cl and G$_{nc}$-Cl(n: generation number).

	Salicyl.[mmol]	FeCl$_3$[mmol]	NEt$_3$ [mmol]	Yield [%]
G$_{0a}$-Cl	15.41	7.04	15.41	55
G$_{1a}$-Cl	6.12	3.06	6.12	28
G$_{2a}$Cl	5.00	2.50	5.00	48
G$_{a3}$-Cl	3.57	1.79	3.57	29

	Salicyl.[mmol]	FeCl$_3$[mmol]	NEt$_3$ [mmol]	Yield [%]
G$_{1b}$-Cl	0.48	0.24	0.48	20
G$_{2b}$-Cl	1.01	0.51	1.01	66.5
G$_{3b}$-Cl	2.80	1.40	2.88	63.9
G$_{4b}$-Cl	5.89	2.94	5.89	15

	Salicyl.[mmol]	FeCl$_3$[mmol]	NEt$_3$ [mmol]	Yield [%]
G$_{1c}$-Cl	10.44	5.22	10.44	45
G$_{2c}$-Cl	3.36	1.68	3.36	71
G$_{3c}$-Cl	5.12	2.56	5.12	18
G$_{4c}$-Cl	7.04	3.52	7.04	13

3. Structure Investigation of the Dendrimeric Compounds

All compounds were characterized by IR spectroscopy and ESI-MS. The IR spectra were measured in KBr matrix on a Brucker Optics Tensor in the 4000-400 cm^{-1} region at ambient temperatures. Infrared spectroscopy has proved to be a very useful tool in the structural analysis and identification of different dendrimeric compounds[8, 9]. For the synthesized amines, the IR spectra show a band in the range of 1654-1645 cm^{-1} characteristic of NH stretching vibrations.For synthesized nitriles, one band appears in the range of 2250-2240 cm^{-1} characteristic of C≡N stretching vibrations, whereas the NH stretching vibrations disappear completely. Vice versa, the C≡N stretching vibration band disappears after the reduction with DIBAL-H.

For synthesized dendrimeric complexes, bands in the range of1618-1621 cm^{-1} are corresponding to the stretching vibration of C=N of the imine group. (See Tab. 3)Selected examples of ESI-MS signals of different dendrimeric compounds are given below in tabular form (see Tab. 3). Due to thehyperbranched 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.

Table 3. Selected examples of infrared spectroscopy bands and electrospray ionisation mass spectrometry (ESI MS) signals of different dendrimeric complexes

	M [g/mol]	υ(C=N) [cm^{-1}]	ESI-MS m/z		M [g/mol]	υ(C=N) [cm^{-1}]	ESI-MS m/z
G_{0a}-Cl	546.87	1619.3	547.1(z =1)	**G_{1b}-Cl**	1115.79	1618.7	1061(z =1)
G_{1a}-Cl	1380.39	1621.5	1337(z =2)	**G_{2b}-Cl**	2472.45	1619.1	1236(z =2)
G_{2a}-Cl	2959.17	1620.7	1479.1(z =2)	**G_{3b}-Cl**	5102.85	1620.2	1595.6(z=3)
G_{3a}-Cl	6124.62	1619.6	1524(z =4)	**G_{4b}-Cl**	10364.02	1620.0	1727.3(z=6)

	M [g/mol]	υ(C=N) [cm^{-1}]	ESI-MS m/z
G_{1c}-Cl	1023.69	1618.7	476.5(z = 2)
G_{2c}-Cl	2037.68	1619.8	1019.3(z = 2)
G_{3c}-Cl	4179.20	1620.2	10358.3(z = 3)
G_{4c}-Cl	8413.85	1620.1	1542.1(z = 5)

4. Mössbauer Results and Discussion

The Mössbauer spectra were recorded using a conventional transmission spectrometer at T = 20 K and T = 300 K. ^{57}Co/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. 6 and Table 4 show the Mössbauer spectra and the parameter of the dendrimeric complexes from zeroth to fourth generation. Mössbauer spectra of all dendrimeric compounds at 300K and at 20 K exhibit the shape of a simple line doublet indicating Fe(III) in high-spin state (S=5/2).

Some spectra could be described best by a fit with 2 or 3 lorentzian doublets. Since one would not expect discrete positions for the iron centres, for both isomeric shift (IS) and quadrupole splitting values the centre of gravity was determined for the complete signal in order to achieve better comparability within this discussion.

At 300 K all spectra exhibit typical values for the IS in the range of 0.237(22)-0.341(13) mm/s. The observed higher values at 20 K are well in accordance with the “Second-Order Doppler Shift” (in the range of0.295(37)-0.440(11) mm/s). There seems to be no consistent trend of an influence of the generation growth on the IS. Deviations of individual values could be caused by agglomeration effects. (See Tab. 4)

The QS values exhibit a slight temperature dependence. Values in a range of 0.554(21)-1.300(30) 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. (See Fig. 5& Tab. 4)

In case of the G_c-Dendrimers strong asymmetry of the Mössbauer doublet is observed (see fig. 6). This asymmetry is particularly pronounced for the first and third generation 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 effect. 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.

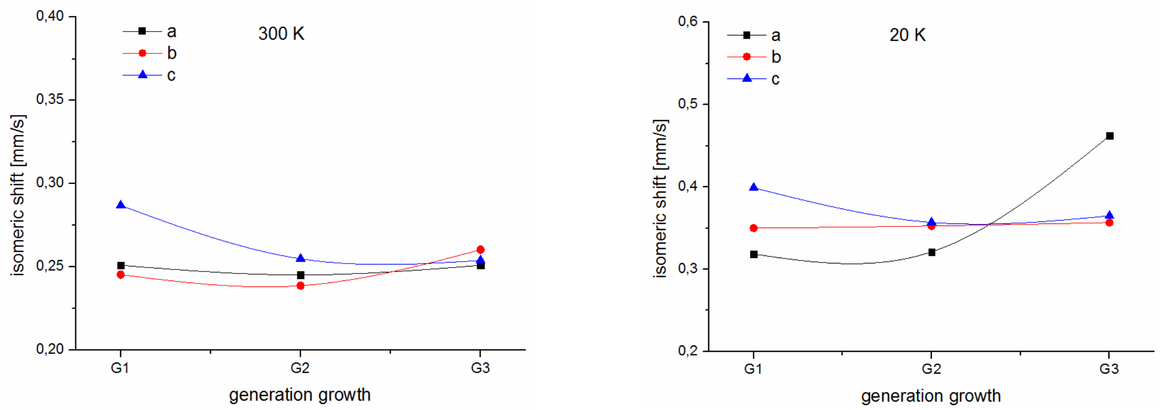


Figure 5. Dependence of the Isomeric shift on the dendremeric cores a, b and c and the generation at 20 K and 300 K..

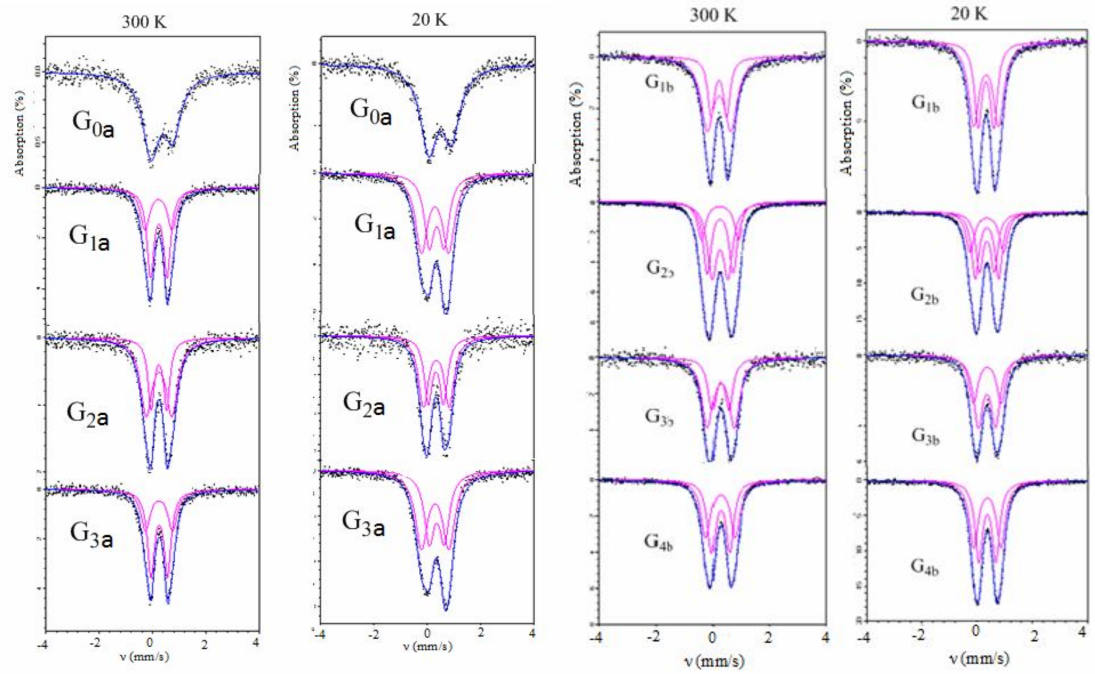


Figure 6a.Mössbauer spectra at 300 K and at 20 K of dendrimeric Iron(III) compound G_{na}, and G_{nb}(n: generation number)

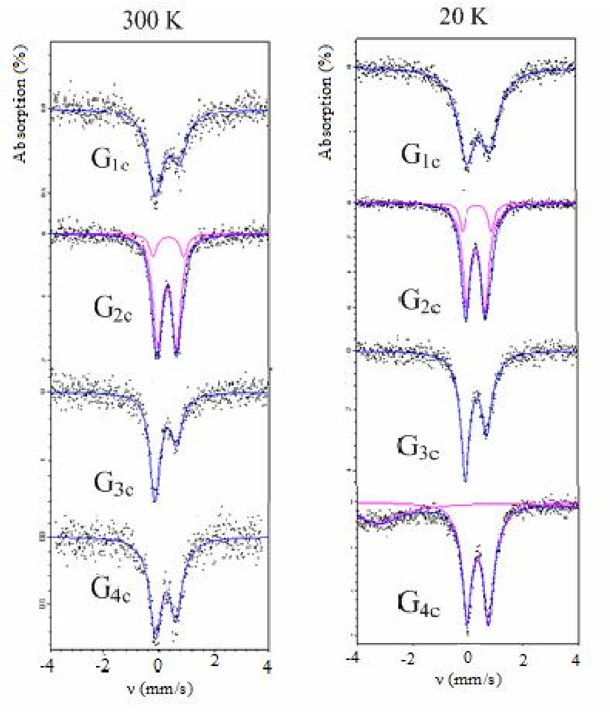


Figure 6b.Mössbauer spectra at 300 K and at 20 K of dendrimeric Iron(III) compound G_{nc}(n: generation number)

Table 4: Mössbauer parameters of dendrimeric Iron(III) compounds G_{na}, G_{nb} and G_{nc} (n: generation number)

		Fe(III) HS-state			Fe(III) HS-state		
Complexes core a	T(K)	δ [mm/s]	Δ [mm/s]	Fraction [%]	δ [mm/s]	Δ [mm/s]	Fraction[%]
G_{0a}-Cl	300	0.341(13)	0.799(18)	100	---	---	---
	20	0.440(11)	0.845(16)	100	---	---	---
G_{1a}-Cl	300	0.2457(67)	1.018(22)	39	0.2558(30)	0.620(19)	61
	20	0.358(17)	0.563(11)	43	0.295(19)	1.024(11)	57
G_{2a}-Cl	300	0.247(13)	0.963(19)	66	0.242(27)	0.587(13)	34
	20	0.341(20)	0.960(24)	57	0.295(14)	1.024(32)	43
G_{3a}-Cl	300	0.245(13)	01.018(17)	39	0.255(12)	0.620(17)	61
	20	0.358(11)	0.563(30)	42	0.547(25)	0.848(15)	57

		Fe(III) HS-state			Fe(III) HS-state		
Complexes core b	T(K)	δ [mm/s]	Δ [mm/s]	Fraction[%]	δ [mm/s]	Δ [mm/s]	Fraction[%]
G$_{1b}$-Cl	300	0.2423(32)	0.554(21)	31	0.2472(37)	0.837(65)	69
	20	0.3402(29)	0.803(43)	59	0.360(25)	0.340(21)	41
G$_{2b}$-Cl	300	0.2373(22)	1.300(30)	20	0.242(12)	0.909(14)	37
					0.2378(14)	0.555(27)	43
	20	0.3552(11)	0.848(15)	39	0.3500(21)	1.215(24)	27
					0.3528(13)	0.535(24)	34
G$_{3b}$-Cl	300	0.2654(59)	0.920(69)	65	0.2524(37)	0.569(52)	35
	20	0.367(12)	1.003(41)	40	0.350(13)	0.626(31)	60
G$_{4b}$-Cl	300	0.2563(15)	0.621(11)	50	0.2545(19)	1.007(20)	49
	20	0.3670(11)	0.6150(19)	50	0.3672(14)	0.982(15)	50

		Fe(III) HS-state			Fe(III) HS-state		
Complexes core c	T(K)	δ [mm/s]	Δ [mm/s]	Fraction [%]	δ [mm/s]	Δ [mm/s]	Fraction [%]
G$_{1c}$-Cl	300	0.287(20)	0.864(33)	100	---	---	---
	20	0.3990(83)	0.921(13)	100			
G$_{2c}$-Cl	300	0.2673(47)	0.696(11)	72	0.315(33)	1.100(47)	28
	20	0.4073(31)	1.100(17)	17	0.3746(24)	0.608(57)	83
G$_{3c}$-Cl	300	0.250(16)	0.755(28)	100	---	---	-----
	20	0.3654(43)	0.8269(78)	100			

5. References

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