



# Reactions of Chromium(III)- and Cobalt(III)-amine-complexes with Starburst(PAMAM)dendrimers

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**Abstract.** The starburst(PAMAM)dendrimer of generation 0 was reacted with pentaamine-triflato-chromium(III) and -cobalt(III). The products were separated by ion exchange chromatography and characterized by elemental analysis, UV-VIS-, IR-,  $^{13}\text{C}$ -spectroscopy or cyclic voltammetry. The dendrimer forms five membered chelate rings containing amine and amide nitrogens and binds one or two metal ions.

**Key words:** starburst(PAMAM)dendrimer, dendrimer complexes

## 1. Introduction

The starburst-polyamidoamine-dendrimer (PAMAM) of generation 0 contains four terminal amine-groups and four peptide links. It has been reported that the starburst(PAMAM)dendrimer binds metal-ions to form chelates [1]. Similar chelate complexes of different peptides with cobalt(III) are also well known [2].

We report on the products of the reaction of the (PAMAM)dendrimer with  $[\text{M}(\text{NH}_3)_5\text{OSO}_2\text{CF}_3](\text{OSO}_2\text{CF}_3)_2$  ( $\text{M} = \text{Co}^{3+}, \text{Cr}^{3+}$ ).

## 2. Experimental Section

**Materials:** starburst(PAMAM)dendrimer of generation 0 was purchased from Aldrich, as a 20% methanolic solution. After evaporation of the solvent it was used without further purification. Sulfolane (Merck, Aldrich) was used after double distillation. The  $[\text{M}(\text{NH}_3)_5\text{OSO}_2\text{CF}_3](\text{OSO}_2\text{CF}_3)_2$  compounds ( $\text{M} = \text{Co}^{3+}, \text{Cr}^{3+}$ ) (2) were prepared as described previously [3]. Ion exchange chromatography was carried out on a Sephadex SPC-25 (40–120 microns) (Aldrich) column with hydrochloric acid as the eluent. All other reagents were of AnalaR grade.

**Spectroscopic studies:** A Cary 2300 (Varian) spectrophotometer was used to measure the UV-Visible spectra. IR-spectra were obtained by a Nicolet 5PC spectrometer. The  $^{13}\text{C}$  NMR spectra were recorded on a Bruker AX300 instrument and the compounds were dissolved in  $\text{D}_2\text{O}$ . Atomic absorption spectroscopy was

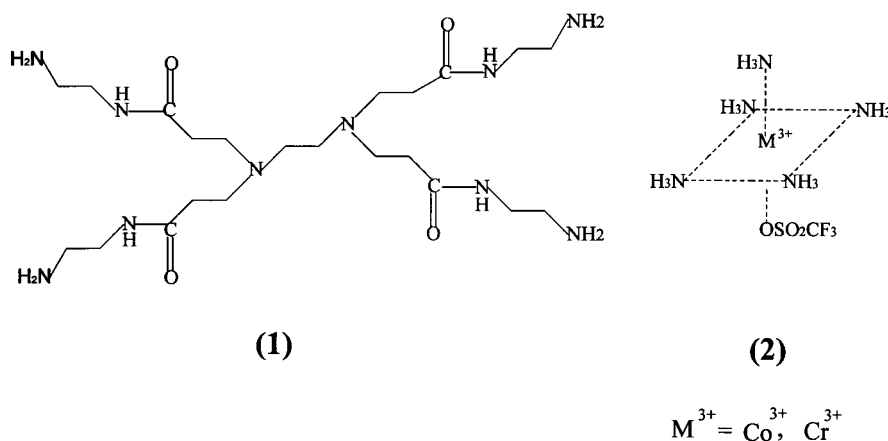


Figure 1. Starburst(PAMAM)-dendrimer (generation 0.) (1) and  $[M(III)(NH_3)_5OSO_2CF_3]-(OSO_2CF_3)_2$  ( $M(III) = Co^{3+}, Cr^{3+}$ ) (2).

carried out on a Techtron AA6 (Varian) while elemental analyses were measured on a CHN-O-Rapid (Heraeus).

Electrochemistry: The cyclic voltammograms were recorded using a BAS MF-9093 system with a Pt working and a Ag/AgCl reference electrode and either 0.1 M  $HClO_4$  or 0.1 M HCl.

### 3. Results and Discussion

The reaction of the starburst(PAMAM)-dendrimer of generation 0. (Aldrich) (1) with  $[M(NH_3)_5OSO_2CF_3](OSO_2CF_3)_2$  ( $M = Co^{3+}, Cr^{3+}$ ) [3] (2) in sulfolane (Figure 1) produced a mixture of various positively charged species which were separated by chromatography on Sephadex SPC-25 with HCl as the eluent. The desired dendrimer complexes could be eluted with HCl concentrations  $> 0.5$  M. They were obtained as glassy solids with colors ranging from deeply red to brown.

Elemental analysis showed dendrimer to metal ratios between one and two and  $Cl^-$  to metal ratios between six and ten. The ratio of nitrogen to dendrimer was 11 to 14. In view of the fact that the ligand itself contains 10 nitrogens it is lower than expected for a dendrimer-pentaammine-metal complex. This indicates that predominantly one metal ion was coordinated to the dendrimer while some of the ammonia ligands of the precursor complex (2) were substituted by further amine or amide groups of the dendrimer. However, some products which contained two metal ions per dendrimer unit were also found. The high content of  $Cl^-$  indicates that the dendrimer nitrogens are protonated and that the products are highly charged.

The various chromatographic fractions had absorption maxima (in 0.1 M  $HClO_4$ ) in the region of 470–480 nm ( $\lambda_1$ ) and 335–345 nm ( $\lambda_2$ ) for the cobalt(III)-compounds and 475–515 nm ( $\lambda_1$ ) and 340–380 nm ( $\lambda_2$ ) for the chromium(III)-

products while the free ligand shows no absorption between 300 nm and 600 nm. The absorption maxima of the cobalt compounds are in the same region as the maxima of the Co(III)-peptide complexes [2]. Both groups of substances should have similar structures because the peptide ligand contains the same functional groups as the dendrimer with the exception of the carboxylate groups. It has been shown that a deprotonation of the amide groups occurs even in acid solution. It increases the strength of the metal-ligand bond [2] which causes a hypsochromic shift of the absorption maxima.

Measurements of the ligand field strength of cobalt peptides led to the following spectrochemical series for the different coordinating nitrogens of the peptide ligand [4]



The dendrimer ligand is stronger than the peptides because it contains more amine groups. It is able to coordinate even chromium(III), a reaction that was not yet reported for the peptides. The IR-spectra showed a very strong and broad band in the region between  $3500\text{ cm}^{-1}$  and  $3000\text{ cm}^{-1}$  ( $\nu(N-H)$  and  $\nu(C-H)$ ) and two strong bands at  $1650\text{ cm}^{-1}$  ( $\nu(C=O)$ ) and  $1560\text{ cm}^{-1}$  ( $\nu(C-N)$ ). These bands are typical for the dendrimer. In addition to these, two new bands appeared at  $1720\text{ cm}^{-1}$  and  $1620\text{ cm}^{-1}$ . They are shifted  $60\text{ cm}^{-1}$  compared to the amide bands of the free ligand. This indicates a coordination of the metal ions through some of the amide groups of the dendrimer. Similar results are reported for the cobalt peptides [5].

The  $^{13}\text{C}$ -NMR-data of the cobalt(III)-compounds in  $\text{D}_2\text{O}$  are shown in Table I. It contains either signals of free dendrimer branches or high-field shifted signals of C(3) to C(6). The highest shift of about 4 ppm shows C(3) while the signals of C(5) and C(6) are shifted by about 3 ppm. This confirms the results mentioned above and indicates that the dendrimer branches coordinate through the amine and amide nitrogens of the peptide links to form chelate complexes. The fact that the chemical shifts of the non-coordinated dendrimer can also be found (see Table I) means that not all of the four dendrimer branches are coordinated to the metal ion.

All these results are consistent with the structure given in Figure 2. It can be seen that one metal ion is bonded by two peptide links in the equatorial plane of the octahedral chelate complex. Most of the described products were coordinated through another amine nitrogen of the dendrimer in the axial level while the other one was connected to an ammonia ligand. Some products also had two ammonia ligands in the axial plane.

The cyclic voltammograms of cobalt(III)- and chromium(III)-dendrimer showed pH-dependent potentials between  $-0.370\text{ V}$  and  $-0.490\text{ V}$  for the reduction and between  $-0.270\text{ V}$  and  $-0.390\text{ V}$  for the oxidation (vs. Ag/AgCl). These compounds coated the surface of the Pt-working electrode very quickly and showed a reduction within the dendrimer-core similar to peptide-complexes [6] and some dendrimers peripherally modified by anion radicals [7].

Table 1.  $^{13}\text{C}$ -NMR-data of the Co-dendrimer-products and of the free ligand in  $\text{D}_2\text{O}$ .

	free dendrimer $\delta$ [ppm]	coordinated $\delta$ [ppm]
C(1)	50,0	50,64
C(2)	49,5	47,78
C(3)	33,1	28,92
C(4)	174,9	172,6
C(5)	40,3	36,79
C(6)	42,1	39,28

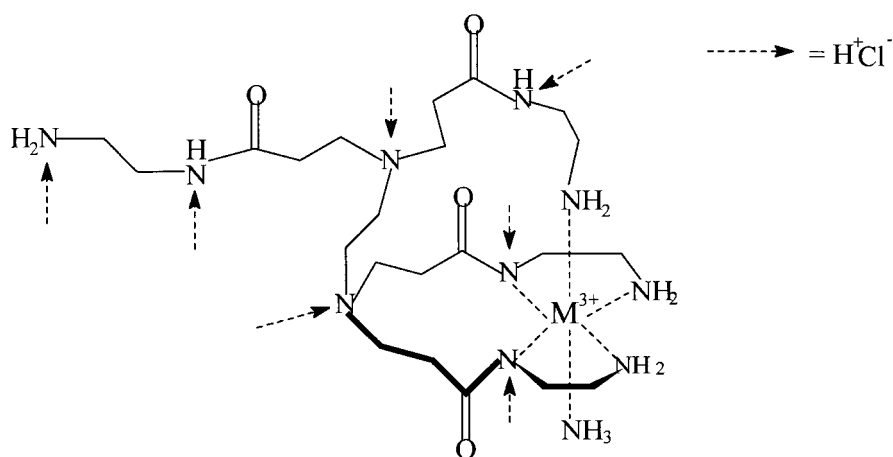


Figure 2. Postulated structure of the main product. (The arrows point to the protonated nitrogens).

**References**

1. M. F. Ottaviani, S. Bossmann, N. J. Turro, and D. A. Tomalia: *J. Am. Chem. Soc.* **116**, 661 (1994).
2. G. Wilkinson, R. D. Gillard, and J. A. Mc Clerverty: *Comprehensive Coordination Chemistry*, v. 4, pp. 682–684 Pergamon Press (1987), and further references given there.
3. N. E. Dixon, G. A. Lawrance, P. A. Lay, and A. M. Sargeson: *Inorg. Chem.* **23**, 2940 (1984).
4. I. G. Browning, R. D. Gillard, J. R. Lyons, P. R. Mitchell, and D. A. Phipps: *J. Chem. Soc. Dalton Trans.* 1815 (1972).
5. E. J. Evans, C. H. Hawkins, J. Rodgers, and M. R. Snow: *Inorg. Chem.* **22**, 34 (1983).
6. S. Fujii, N. Tatsumoto, and K. Yamaoka: *J. Electroanal. Chem.* **16**, 193 (1986).
7. I. Tabakovic, L. L. Miller, R. G. Duan, D. C. Tully, and D. A. Tomalia: *Chem. Mater.* **9**, 736 (1997).

