3-D Water-Soluble Reversible Neodymium(III) and Lanthanum(III) Coordination Polymers

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The formation of soluble supramolecular 3-D coordination polymers with Nd^{3+} and La^{3+} in aqueous solution has been studied for two bifunctional ligands consisting of two pyridine-2,6-dicarboxylate groups connected at the 4-position by $O(CH_2CH_2O)_4$ and $O(CH_2CH_2O)_6$ spacers (**C4** and **C6**, respectively). Viscosity measurements were used to monitor the network formation as a function of the ligand concentration, and the ratio between metal ions and ligands. For corresponding conditions **C4** solutions with Nd^{3+} always gave much higher viscosities than **C6** solutions with Nd^{3+}. **C6** is long, and flexible enough to bind with both chelating groups to only one metal ion (ring formation). This causes the polymers to stop growing, resulting in smaller average sizes of the 3-D polymers. The ring-structures could be demonstrated by ^1H NMR spectroscopy using **C6** and La^{3+} at low concentrations.

Introduction

In the past few decades, the field of supramolecular chemistry has grown into an important part of chemistry. Supramolecular structures can be built using several noncovalent intermolecular interactions such as hydrogen bonding, π−π-stacking interactions, van der Waals interactions, and coordinative bonding (metal−ligand bonding).[1]

Metal−ligand bond strengths span a wide range, with the strength depending on both the metal ion and the ligand. In some cases the bond strengths are comparable to covalent bonds, and the reversibility of the binding can be tuned by the choice of solvent.[1] When a coordinating solvent such as water or acetonitrile is used, the reversibility of the binding increases.

In a previous study, we reported the reversible formation of linear polymers in aqueous solutions of Zn^{2+} ions with bifunctional ligands, consisting of two terdendate pyridine-2,6-dicarboxylate groups connected through an $O(CH_2CH_2O)_4$ or $O(CH_2CH_2O)_6$ spacer, **C4** or **C6**, respectively.[2] The bifunctional ligands can form not only linear polymers through metal ion coordination, but also rings. The rings can be formed by one ligand molecule and one metal ion (monomer rings) if a long and flexible spacer links the ligand groups. If the spacer is shorter or less flexible, at least two ligand molecules and two metal ions are necessary to form rings (dimer and larger rings). We showed, that the amount of ring formation depends on spacer length, concentration, temperature, and the metal ion/ligand molecule (M/L) molar ratio.[2] The total amount of rings is much higher when the ligand is long enough to form monomeric rings than when only dimers and larger rings can be formed. The larger the rings become, the smaller the probability of them being formed. This implies, that the amount of small rings will always be higher than the amount of large rings. When the molecules are able to form monomeric rings, there will still be dimer and larger rings present in solution, but their relative amounts will be much smaller. This also means, that when two ligand molecules differing in spacer length are compared, the solutions with molecules able to form monomeric rings will show a greater overall formation of rings than the solution with molecules able to form only dimer and larger rings.

The rings are dominant at low concentrations, where the probability of meeting a ligand group of another molecule is smaller than at higher concentrations. On going from a low to a high concentration, mainly rings are formed in the first instance and, after reaching a critical concentration, linear polymers are formed in addition. The total amount of rings stays approximately the same, but the amount and average length of the linear polymers increases. By considering the relative amounts we can say, that rings play an important role at low concentrations, but can be ignored at high concentrations. This relation between the formation of rings and linear chains was also found for reversible hydrogen-bonded supramolecular polymers.[3]

Another very important role in the equilibrium between rings and linear polymers is the molar ratio between metal

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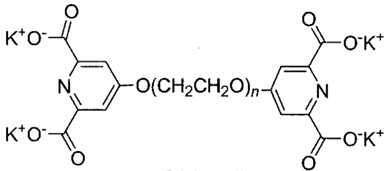
ions and ligand molecules (M/L). The ideal ratio for forming linear polymers is 1, but this is also the ideal ratio for ring formation. Overall it can be said, that the influence of rings is largest at a molar ratio of unity and at low concentrations.[2]

In the field of coordination chemistry, interest in the lanthanide metal ions has grown considerably in the last two decades. Because of their large size, lanthanide ions can generally support higher coordination numbers than transition metal ions. Not many self-assembled structures of lanthanide ions in aqueous solution have been reported, although some lanthanide-containing helicates in water have been reported.[4−6] A few lanthanide coordination polymers having 3-D networks have also been reported, but only solid-state properties have been studied.[7−11]

In this paper we describe the reversible formation of 3-D polymers of the bifunctional ligands **C4** and **C6** with Nd^{3+} and La^{3+}. Neodymium(III) and lanthanum(III) are both lanthanide ions, and are large enough to form complexes with three terdendate ligands (9-coordination).[12] Compared with first-row transition metal ions such as Zn^{2+} or Ni^{2+}, which give 6-coordination with terdendate ligands, Nd^{3+} and La^{3+} can bind an additional ligand group by self-assembly, which makes the formation of a 3-D network possible. Additionally, we show that the possibility of ring formation also plays an important role in this system.

Results and Discussion

The ligands we used were **C4** and **C6**, these are represented in Figure 1. The complexing groups are based on 2,6-pyridinedicarboxylic acid. The complexation behavior of this group has been well studied with numerous metal ions. The complexation constants (p*K*) of the subsequent bindings of three 2,6-pyridinedicarboxylic acid molecules to one Nd^{3+} ion are 8.78, 6.72, and 5.06 as reported by Grenthe.[13]



C4 (*n* = 4)
C6 (*n* = 6)

Figure 1. Schematic representation of the bifunctional ligands **C4** and **C6**

In our study we did not verify these stability constants but only the stoichiometry of binding. This was done using a monofunctional ligand with only an ethoxy group at the 4-position of the pyridine moiety in an isothermal titration calorimetric experiment (ITC). As can be seen in Figure 2, an inflection point was found at an Nd^{3+}/monoligand molar ratio of 0.33. This experiment confirms, that the Nd^{3+} center is surrounded by three terdendate monofunctional ligands.

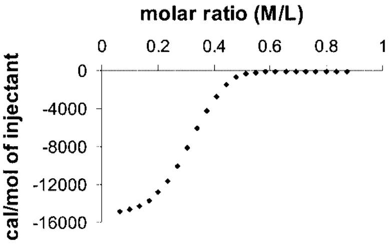


Figure 2. ITC curve of the monofunctional ligand 4-ethoxy-2,6-pyridinedicarboxylic acid (1.07 mM in cell) and $Nd(NO_3)_3$ (9.65 mM in burette) in a 0.1 M PIPES buffer of pH = 5.4 at 298 K

In a previous paper we showed, that **C4** and **C6** display different behavior towards Zn^{2+} although they differ only in spacer length $[O(CH_2CH_2O)_4$ versus $O(CH_2CH_2O)_6]$.[2] One **C6** molecule is just long enough to form a ring around one zinc ion (monomer ring). On the other hand **C4** cannot form a monomeric ring, and needs at least two ligand molecules and two zinc ions to form a ring. This implies that the total amount of rings formed is much higher when **C6** is used instead of **C4** at all concentrations, as explained in the Introduction.

The situation is different when Nd^{3+} was used instead of Zn^{2+}. The ligands still form rings with the metal ion, and **C6** more so than **C4**, but the metal ion has still one binding site left. This makes the system more complicated. Although monomer rings alone will not be present anymore, they can act as chain stoppers as shown in Figure 3. **C4** is shorter, and therefore similar chain-stopping rings cannot be formed. The smallest possible rings do not prevent the polymer from growing longer as shown in Figure 3.

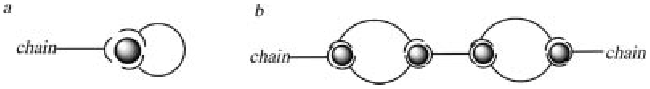


Figure 3. Schematic representation of the smallest possible rings for **C6** (a) and **C4** (b), and their influence on polymer formation

Viscosity measurements were used to study the solution properties as a function of the molar ratio. We titrated a ligand solution in a 0.1 M PIPES buffer of pH = 5.4 with an $Nd(NO_3)_3$ solution in the same buffer. A precipitate was always initially formed upon the addition of neodymium ions, but this completely dissolved after mixing. After each addition the viscosity was measured. Above an M/L molar ratio of 1, the precipitate did not dissolve anymore, and no viscosities could be measured above that ratio. At much larger ratios (M/L > 2) the precipitates dissolved easily again upon shaking. In Figure 4 the reduced viscosity of **C4** and Nd^{3+} has been plotted as a function of the molar ratio at three different concentrations of ligand (20.0 mm, 36.7 mm and 53.6 mm). We found a peak in the viscosity at

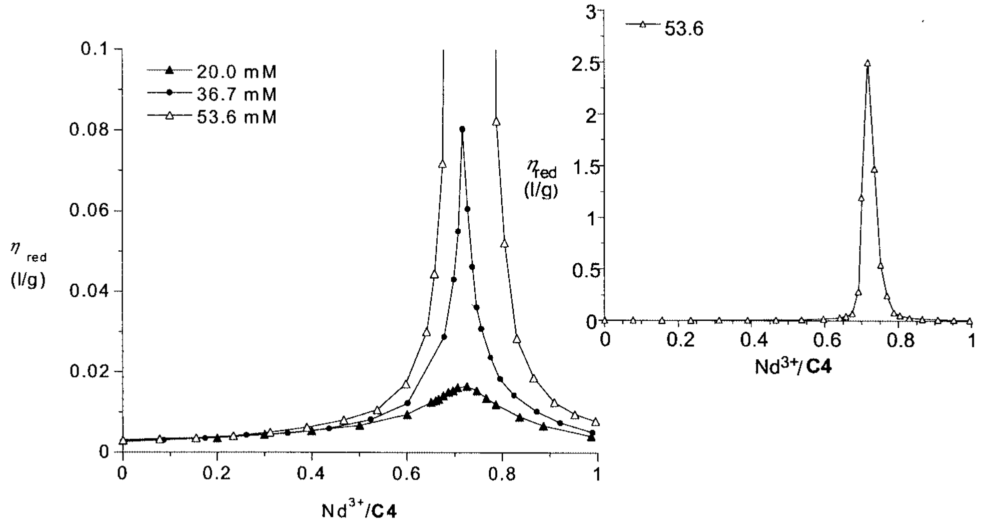


Figure 4. Reduced viscosity of **C4** as a function of molar ratio $Nd(NO_3)_3$/**C4** in a 0.1 M PIPES buffer of pH = 5.4 at 298 K at different concentrations

a molar ratio of about 2:3 (M/L), which can be expected when mixing a bifunctional ligand with a metal ion capable of binding three ligand groups. However, the most noticeable fact is the enormous effect of concentration. At the lowest concentration (20 mM), the highest reduced viscosity was 0.017 L/g. When the concentration was increased further to 37.6 mM, the highest reduced viscosity was already 0.071 L/g, and when the concentration was increased to 53.6 mM, the reduced viscosity went up to at least 2.5 L/g. This shows, that the size of the aggregates increases enormously with concentration through the formation of 3-D networks. The presence of a peak indicates, that the process is reversible. An excess of metal ions (> 0.67) causes the network to break down.

Upon close inspection of the graphs it can be seen, that the peak is shifted a little compared to the 2:3 ratio. With increasing concentration, the peak shifted to a slightly higher molar ratio. We will explain this after discussing the viscosity plots of **C6**.

Figure 5 shows the viscosity of **C6** and Nd^{3+} as a function of molar ratio at four different concentrations. Most noticeable here is, that although the viscosity increases with increasing concentration, this effect is much smaller than observed for **C4**. The curves are also much more asymmetric than those of **C4**. Another effect is the clear shift of the peak to higher molar ratios with increasing concentration. This shift is larger than for **C4**. The shifts of the peaks are plotted in Figure 6 for both ligands as a function of concentration.

The explanation for the low viscosity, asymmetric curves, and the large shift of the peak of **C6** compared with that of **C4** can only be found in the much stronger tendency of **C6** to form small rings. Since **C6** is able to form monomeric rings, which can act as chain stoppers (see Figure 3a), the structures cannot grow as large as for **C4**. This causes the much lower viscosity of **C6** and Nd^{3+} at all concentrations. The ideal molar ratio for formation of those rings is 0.67. At larger molar ratios (M/L), the amount of the rings de-

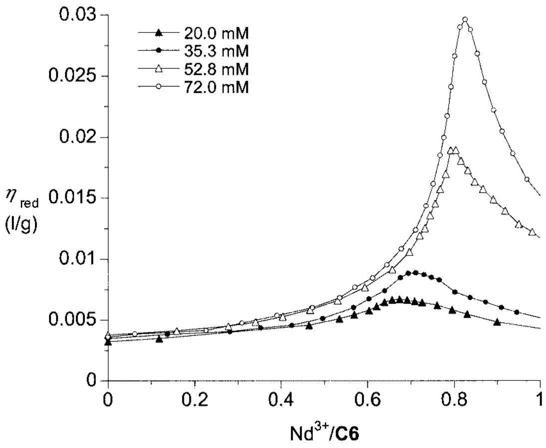


Figure 5. Reduced viscosity of **C6** as a function of molar ratio $Nd(NO_3)_3$/**C6** in a 0.1 M PIPES buffer of pH = 5.4 at 298 K at different concentrations

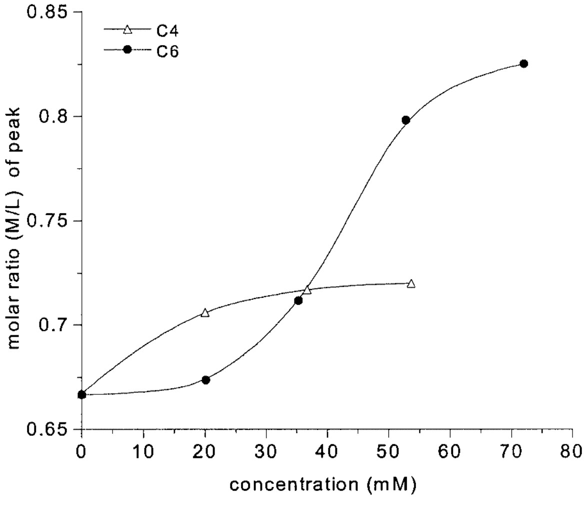


Figure 6. Molar ratio at the highest viscosity of solutions of **C4** and **C6** with Nd^{3+} as a function of concentration

creases, allowing the formation of longer chains, and therefore the highest reduced viscosity is reached at higher molar ratios. This also explains the asymmetric curves. At higher molar ratios (above 0.67) the rings open and become part of the 3-D polymers. This effect contributes to higher viscosities. At these higher molar ratios, however, the metal ions will not all be coordinated to three chelating groups, which causes the viscosity to drop. Both effects counteract each other, leading to a slower decrease in viscosity than expected based on only the explanation of the excess of metal ions.

C4 also shows a shift in the viscosity peak, but it is much smaller. The origin of the shift here can, however, not be found in end capping by ring formation, since the rings can be part of a polymer chain (see Figure 3b). Therefore, the shift found for **C4** has an explanation different from that for **C6**. The shift for **C4** may be explained by the fact, that more expanded structures can be formed when not every metal ion is complexed with three ligand groups. This expansion causes a higher viscosity even though the molar mass of the structures is not larger. This is also the case for conventional covalently bonded polymer solutions. Expanded polymers take a larger volume, and therefore their solutions give higher viscosities than solutions of polymers with the same length but which are more compact.

For **C4**, a concentration-dependent viscosity plot was also measured at a constant M/L molar ratio of 0.71, corresponding to the average molar ratio of the top of the peak at concentrations above 20 mM. Although the top of the peak for concentrations below 20 mM is lower than at M/L = 0.71, the influence of this is negligible due to the broadness of the peak at lower concentrations. This plot is shown in Figure 7 to illustrate the enormous effect of concentration on the viscosity, and thus on the sizes of the self-assembled structures. With increasing concentration, the influence of the rings becomes smaller, and the 3-D polymers become larger, resulting in the steep increase in viscosity (see Figure 8).

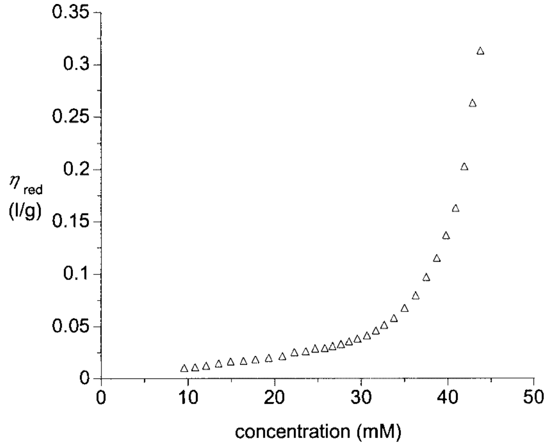


Figure 7. Reduced viscosity of **C4** as a function of concentration at a $Nd(NO_3)_3$/ligand ratio of 0.71 in a 0.1 M PIPES buffer of pH = 5.4 at 298 K

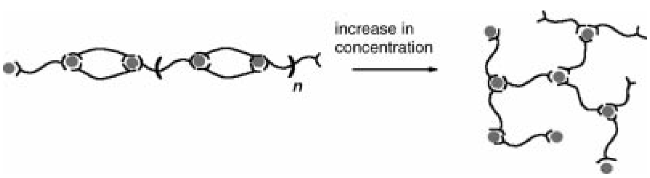


Figure 8. Changes in the structures of **C4**/Nd^{3+} coordination aggregates as a function of concentration

Some NMR experiments were performed in order to examine more closely the shifts of the peaks in the viscosity plots with respect to the molar ratio. The different causes for the shifts for **C6** and **C4** can be illustrated by ^1H NMR experiments. These experiments were performed using lanthanum(III) as the metal ion instead of neodymium(III), because neodymium broadens the signals in the spectrum; La^{3+} has properties similar to those of Nd^{3+}. They both belong to the lanthanides, and are known to exhibit 9-coordination.[12,13] The stoichiometry was checked by isothermal titration calorimetry and indeed showed, that three ligand groups are bound to one lanthanum ion. The curve was less steep than that shown in Figure 2 for neodymium due to lower complexation constants, which is in agreement with reported values in the literature. The reported complexation constants (p*K*) of La^{3+} with three dipicolinic acid molecules (structure of complexing group similar to the ones we use) are 7.98, 5.81, and 4.27.[13]

The reduced viscosity plots of both metal ions gave comparable results for both ligand molecules. At the measured concentrations, the shift in the molar ratio of the peak was found for both Nd^{3+} and La^{3+} and for both ligands. However, the viscosity of **C4** with lanthanum was found to be lower than for **C4** with neodymium at a concentration of 36.7 mM (Figure 9).

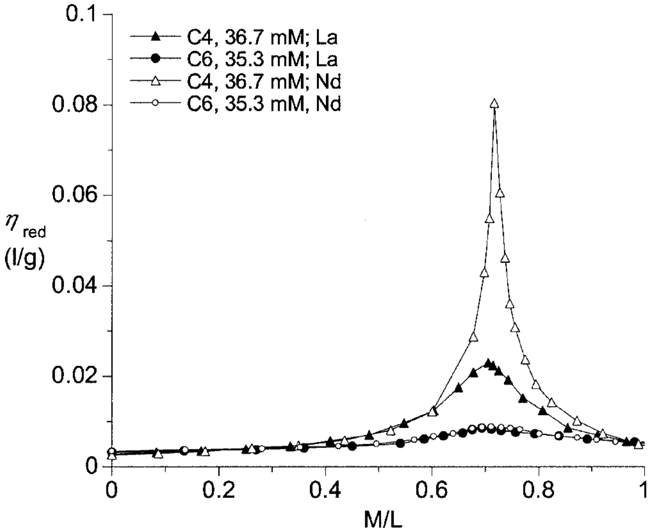


Figure 9. Reduced viscosity of **C4** (triangles) and **C6** (circles) as a function of molar ratio $Nd(NO_3)_3$/ligand (open) and $La(NO_3)_3$/ligand (full) in a 0.1 M PIPES buffer of pH = 5.4 at 298 K

The NMR spectra in D_2O were recorded for both ligands as a function of concentration at an M/L ratio of 0.71, and as a function of the M/L ratio at a ligand concentration of 40 mM. A precipitate was also formed upon addition of La^{3+} ions to a ligand solution, but this subsequently dissolved after mixing. For ligand **C4** few changes occurred in the spectra when metal ions were added to a 40 mM solution in D_2O at pH = 5.8 (Figure 10). The signals between δ = 3.0 and 4.5 ppm originate from the OCH_2 protons in the spacer, the signal at $\delta \approx 7.4$ ppm originates from the aromatic protons in the pyridine ring. The signals became a little broader upon addition of La^{3+} ions, but no new signals appeared. The aromatic signal at δ = 7.35 ppm also shifted to 7.45 upon complexation, up to a molar ratio of 0.72. Above that ratio, the signal shifted back to δ = 7.40 ppm. The proton signals of the spacer shifted a little to high field. The broadening of signals instead of the formation of separated signals for free and coordinated ligand upon addition of metal ions, points to an exchange process between the ligand molecules at a moderate rate on the NMR time scale.[14]

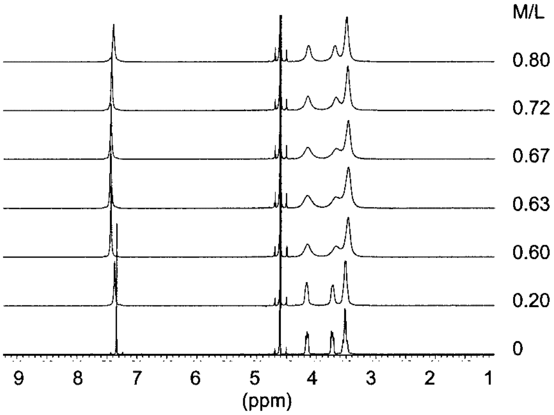


Figure 10. ^1H NMR spectra of compound **C4** with La^{3+} at 40 mM in D_2O at 298 K, pH = 5.8 at various molar ratios

No significant changes occurred in the ^1H NMR spectra upon dilution of a solution with a constant M/L ratio of 0.71 in D_2O (see Supporting Information). This implies that at all concentrations either the exchange between different species is fast, or that only one kind of species (3-D polymer) is present.

For **C6**, a new signal appears both in the molar ratio dependent spectra (Figure 11), and in the dilution spectra (Supporting Information). We observed the new signal as a broad bump in the molar ratio dependent series at δ = 3.1 ppm, with the highest intensity at a molar ratio of 0.67. The highest amount of small ring-like species would be expected at a molar ratio of 0.67, which is the ideal ratio for ring formation around metal ions with 9-coordination. These small structures containing many rings could, for example, look like the representation in Figure 12.

We indeed observed, that upon increasing the molar ratio, the bump became bigger up to a molar ratio of 0.67. This signal in the NMR spectrum is, therefore, most likely caused by the structure of the rings. At higher ratios the height of the bump decreased rapidly because here, larger open structures are more dominant. The larger structures do not seem to give unique signals; they cause only broadening and slight shifting of the signals, which are also present without metal ions. The broadening of the signals is itself an indication of the formation of large structures. The disappearance of the "ring signal" at δ = 3.1 ppm at M/L > 0.67 is in agreement with the viscosity plots. Here the viscosity increased at a molar ratio of > 0.67 due to the opening of ring structures, which contribute to larger structures with higher viscosities.

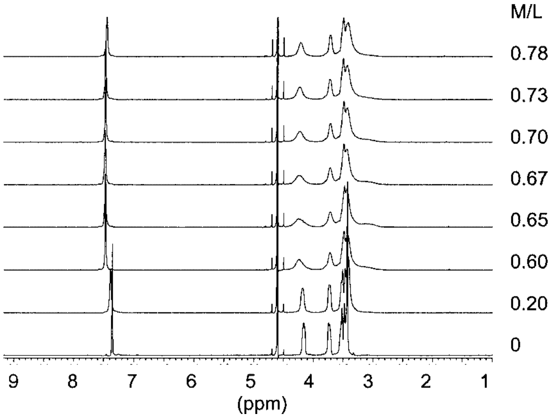


Figure 11. ^1H NMR spectra of compound **C6** with La^{3+} at 40 mM in D_2O at 298 K, pH = 5.8 at various molar ratios

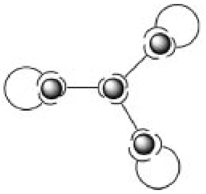


Figure 12. Schematic representation of an example of a small structure containing multiple rings, that can be formed by **C6** and La^{3+} ions at low concentrations and a molar ratio (M/L) close to 0.67

Since we did not see this "ring signal" in the NMR spectra of **C4**, the presence of these kinds of structures can be ruled out here. This is logical, because **C4** is not long and flexible enough to act as a chain stopper.

In the dilution series (Supporting Information) no clear signal was found at δ = 3.1 ppm at 40 mM, but a broad bump appeared starting from about 20 mM, which became resolved into two peaks at 5 mM. Upon dilution, the only species that can become dominant in this system are chain-stopping rings. At low concentrations, the probability of a ligand meeting another metal ion is small, and therefore more rings are formed using only one metal ion to bind both chelating groups of a ligand molecule.

Conclusions

We have reported here the first water-soluble lanthanide-containing reversible 3-D coordination polymers, and the viscosities of their aqueous solutions as a function of both the concentration and the M/L molar ratio. The investigated bifunctional ligands self-assemble in aqueous solution in the presence of neodymium and lanthanum ions to give reversible networks. The use of these ligands in combination with lanthanide ions gives rise to much higher viscosities than when transition metal ions such as zinc are used, that yield linear coordination polymers.[2] A comparison of the viscosities and ^{1}H NMR spectra of **C4** and **C6** shows, that under the same conditions, **C6** always gives smaller structures with lanthanide ions than **C4**. Ligand **C6** has a long enough spacer to bend around one metal ion. In this way it can act as a chain stopper, which causes the structures to stop "growing" and remain small. The ideal M/L ratio for formation of these rings is 0.67. The opening of the rings at higher M/L ratios causes a rather asymmetrical curve, and a shift of the peak in the molar ratio dependent viscosity plots. The ring structures can also be seen in the ^{1}H NMR spectra of **C6** at low concentrations, and at a molar ratio close to 0.67, giving separate signals at $\delta \approx 3.1$ ppm. The ^{1}H NMR spectra of **C4** do not show this signal at any concentration or molar ratio. Also, in the viscosity plots, the shifts of the peaks with respect to the molar ratio are much smaller and the curves are more symmetrical, showing that rings acting as chain stoppers are not present. Coordination structures formed by **C4** and neodymium are therefore able to become much larger. The small shifts of the viscosity peaks here originate from expansion of the structures when metal ions are only slightly in excess.

Experimental Section

The syntheses of compounds **C4** and **C6** have been reported in a previous paper.[2] All commercial chemicals were obtained from Acros or Aldrich, and were used as received. ^{1}H NMR (200 MHz) spectra were recorded with a Bruker AC-E 200 spectrometer. Isothermal titration calorimetry measurements were performed with a Microcal MCS ITC with a cell volume of 1.353 mL. The experiments were performed using injections of 5 µL, 250 s between injections, and a reference offset of 60%. Viscosity measurements were performed in a 100 mM 1,4-piperazinebis(ethanesulfonic acid) buffer (PIPES) of pH = 5.4 with a Schott AVS 360 capillary viscometer. The reduced viscosity is defined as the specific viscosity divided by the ligand concentration C in g/L, i.e. $\eta_{red} = \eta_{sp}/C = (\eta_s - \eta_o)/(\eta_o \cdot C)$, with η_s being the viscosity of the sample, and η_o the viscosity of the solvent.

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