

Supramolecular Polymer Formation by Metal–Ligand Complexation: Monte Carlo Simulations and Analytical Modeling

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Abstract: Equilibrium metal–ligand complexation leading to formation of linear or ringlike supramolecular polymers is studied by means of Monte Carlo (MC) simulations and theoretical analysis. We found that in most of the cases high-molecular-weight polymers are formed over a rather narrow composition range (near the 2:1 ligand–metal ratio). Besides the imbalance in the number of metals and ligands, the molecular weight decrease in the metal-rich area is caused by an increase in 1:1 ligand–metal complex formation. The results of simulations and theoretical modeling show that the fraction of 1:1 complexes considerably decreases for metal–ligand pairs with a high cooperativity of complexation. On the basis of our analytical model, we suggest a simple criterion for choosing the metal/ligand pair to achieve high molecular weight complexes in a broad range of metal-rich compositions. Dilution of a solution of metallosupramolecular polymers is found to decrease the average molecular weight and to enhance ring formation, which otherwise is very limited.

1. Introduction

One of the recent developments in supramolecular chemistry is the application of reversible metal–ligand complexes for creation of new materials with advanced (photochemical,¹ electrochemical,^{2,3} and catalytic⁴) properties.^{5–8} Another advantageous feature of these materials is their self-healing capability.^{5,8–10} The formation of the metallosupramolecular complexes can be reversed, for example, by changing the solution pH or applying electrochemical or thermal changes.^{5,9,10} This opens a unique opportunity for creating new materials with advanced properties that can be manipulated by changing external parameters. The objective of the present research is to aid ongoing experimental efforts by providing a theoretical insight to the basic principles of metal–ligand self-assembly.

As a result of the considerable interest in this field, a range of ligands capable of complexation with various metals have been synthesized.^{3,5,6,10–14} Considerable progress has been

achieved with 2,2':6',2''-terpyridine^{5,7,13,15} as a chelating ligand for a variety of transition metal ions. This ligand enables the construction of a variety of different architectures, such as linear coordination polymers,^{5,13,16} AB and ABC block copolymers, and metallosupramolecular micelles,^{7,17} cross-linked systems,^{11,18} star-shaped^{5,12} and grafted structures.^{5,19} Linear coordination polymers with flexible spacers, which is the main subject of the present paper, have been experimentally obtained for different metal ions, such as Fe(II), Zn(II), Ni(II), Cu(II), and Co(II),^{16,20,21} some of them with chiral precursors. Coordination polymers with a rigid linker have been reported for Ru(II) and Fe(II) ions.^{5,13}

Despite the considerable interest in metallosupramolecular polymers, their physical characterization and experimental

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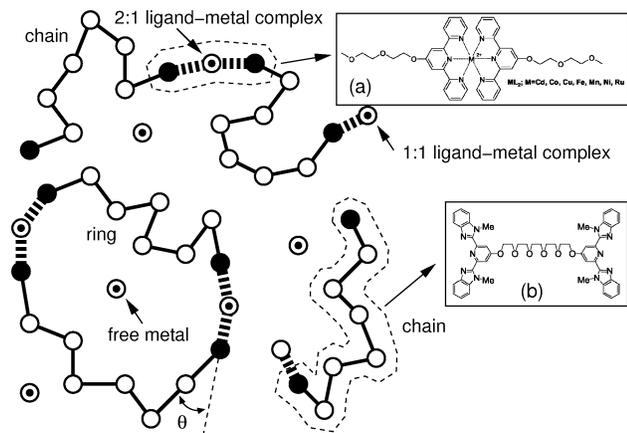


Figure 1. Schematic presentation of metallosupramolecular polymers. Experimental examples of the ligands are shown in insets: (a) from ref 22; (b) from ref 11.

analysis of properties is still in an early stage of development.^{5–7,22} The reason for this is the internal complexity of the self-assembly by metal–ligand complexation. One of the problems encountered is low solubility of rigid metallosupramolecular polymers^{5,13} and a limited range of compositions where high molecular weight complexes can be achieved. Determination of the molecular weight of the polymers (and experimental characterization in general) is a complicated problem itself since the reversible nature of the interactions does not permit (or considerably limits) usage of some traditional techniques.^{3,16,20} Even when the experimental measurements are successful (as for example in viscosity measurements), it is still a challenging task to compare the results for different metal ions or ligands obtained by different (or the same) research groups. The considerable difference in the kinetics and thermodynamics of complexation for different metal–ligand pairs can mask the common trends of self-assembly. The influence of composition or temperature on self-organization of metallosupramolecular polymers (altering chain–ring equilibrium)^{10,23} adds to the complexity of the problem.

So far theoretical and computer modeling has been concerned with reversible association of either donor–acceptor type or binary (or multiple) complex formation of end-functional groups.^{24–28} We are not aware of any theoretical research considering metal–ligand complexation or reversible association of end-functionalized polymers with different energies for the first and second bond formation. The aim of the present research is provide theoretical guidance on the main features of thermodynamically driven self-assembly of metallosupramolecular polymers. We will analyze by means of combined computer and analytical modeling the reversible self-assembly of linear oligomers end-functionalized by ligands capable of forming 2:1 complexes with metal ions (which mediate the polymerization process as shown in Figure 1). Computer simulations will help

to provide the microscopic details of the self-assembly, which are not readily available from experiment (such as ring fraction, influence of rigidity, concentration, and so on) and will serve as a test of the accuracy of our analytical approach. The analytical model based on chemical equilibrium equations will be used to analyze the simulation results and to make predictions on how to obtain high molecular weight polymers over a large composition range by using metal–ligand complexation. These predictions can be used to guide the selection of appropriate metal–ligand pairs in experimental research. We will also analyze the factors influencing formation of linear chains (or rings), compare our results with existing experimental data, and make predictions concerning the general rules of the self-assembly and ways to achieve high-molecular weight complexes.

2. Computational Details

To study the reversible association between linear oligomers end-functionalized for ligand–metal complexation, we apply Monte Carlo (MC) simulations. A metal is assumed to be capable of complex formation with up to two ligands, such that the possibility of branching and gelation is eliminated and only linear chains or rings can be formed. We use the bond fluctuation model²⁹ (BFM) to simulate metals and oligomers of eight monomers each (including end ligands) on a three-dimensional cubic lattice with lateral size $L = 64a$ with periodic boundary conditions. The number of polymer chains was kept constant ($N_0 = 256$), whereas the number of metal ions (N_m) was varied. Each monomer or metal occupies one cell of the lattice of size a . In consideration of excluded volume, the distance between any bonded monomers or between a bonded monomer and a metal can be one of the values $2a$, $\sqrt{5}a$, $\sqrt{6}a$, $\sqrt{7}a$, $3a$, or $\sqrt{10}a$. Having no other interactions between monomers or metals, this corresponds to the good solvent condition (even though the solvent particles are not explicitly modeled) where the radius of gyration for a free oligomer scales with the number of monomers in an oligomer as $R_g \approx N^{0.55}$.

We assume the free oligomers to be absolutely flexible, so there is no penalty for bending any of the chemical bonds connecting the monomer units of an oligomer. Because metal–ligand interactions are orientationally specific there will be a penalty, $E_{st} = K(1 - \cos \theta)$, for bending a reversible bond, where θ is the angle characterizing deviation from linearity, as illustrated in Figure 1. In our simulations we choose the rigidity constant $K = 5kT$, which results in the same Boltzmann factor in the partition function as restricting the bond angle θ to the range $0 < \theta < \theta_{\max} \approx 37^\circ$ and amounts to a loss of entropy per reversible association of $\Delta S \approx 1.525$ (in units of the Boltzmann factor k) per 1:1 ligand–metal complex. For 2:1 complex the corresponding entropic loss will be much larger, as it involves three different bond angles. As to the enthalpy of association, formation of mono ligand–metal (1:1) complex lowers the energy of the system by ΔE_1 and for the bis complex (2:1) by $\Delta E_2 + \Delta E_1$. Below we will use the absolute values of enthalpies to characterize the complex formation. We will introduce cooperativity as a measure of the strength of the second ligand–metal bond compared to the first one: $\Delta E_2 - \Delta E_1$. We will consider the cases of noncooperative association when the first and the second bond are of the same strength ($\Delta E_1 = \Delta E_2$) and cooperative association $\Delta E_2 > \Delta E_1$. We note that apart from cooperativity we did not consider the influence of electrostatic interactions (or counterion distribution) on the properties of the supramolecular polymers (that will be the subject of our future work). Therefore, our results correspond to the case of good solutions of supramolecular polymers with salt-screened electrostatic interactions.

To calculate the properties of the model system defined above, we perform Monte Carlo simulations with two types of updates: moving

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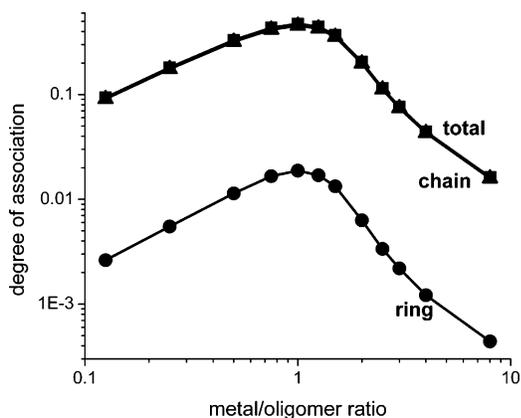


Figure 2. Composition dependence of the average degree of association (fraction of 2:1 complexes) for chains, rings and total for noncooperative metal–ligand complexation $\Delta E_1 = \Delta E_2 = 8kT$. Due to the small ring fraction, the total degree of association practically coincides with the chain fraction in the plot.

attempts of monomers or metals (by use of the Metropolis algorithm³⁰) and bonding update for the ligands.²⁸ For the latter, after the moving attempt for an oligomer end group, a reversible bond (if any) is assumed to be broken and a new bond is rechosen from all possible ones with probabilities given by their respective Boltzmann weights. For each system realization we perform a series of moving attempts and bonding updates until the system reaches equilibrium, at which point the number of reversible bonds and molecular weight distribution are counted and averaged separately over the series of system configurations generated.

3. Results and Discussion

Ring–Chain Equilibrium. One of the important characteristics of a self-assembling polymer system is the degree of association. For metallosupramolecular polymers under consideration the self-assembly occurs by mean of formation of 2:1 ligand–metal complexes. Besides the overall amount of 2:1 complexes, we can also distinguish between the ones belonging to topologically different species: linear chains and rings. For each MC time interval, we count and average separately the number of rings R_i and the number of chains C_i for polymers consisting of i oligomers. The total number of 2:1 complexes in the system is given by

$$\sum_{i=1}^{\infty} iR_i + (i-1)C_i \quad (1)$$

Equation 1 takes into account that a ring of size i contains i 2:1 complexes while a chain of the same size contains only $i-1$ complexes. We define the average degree of association for rings as the ratio of the number of 2:1 complexes in rings to the initial number of oligomers: $f_r \equiv \sum_{i=1}^{\infty} iR_i / \mathcal{N}_0$ and the average degree of association for chains correspondingly as $f_c \equiv \sum_{i=1}^{\infty} (i-1)C_i / \mathcal{N}_0$. The overall degree of association p for the system is given by $p = f_r + f_c$.

Figure 2 shows the total degree of association p along with the degree of association for chains and rings (f_r and f_c) as functions of the composition (i.e., ratio of metals to oligomers) for the case of noncooperative association (i.e., when the energy gain for the metal association with the first and the second ligand is the same $\Delta E_1 = \Delta E_2 = 8kT$). As is seen, the fraction of 2:1

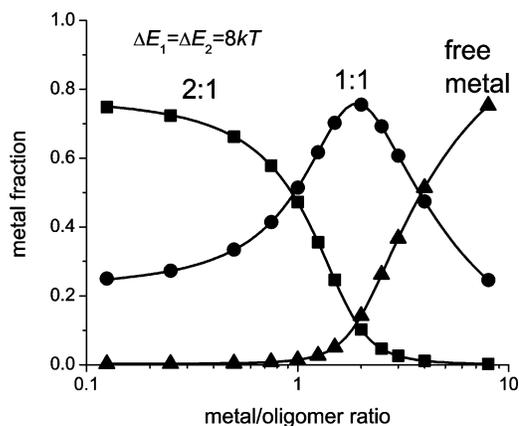


Figure 3. Composition dependence of the average fraction (with respect to the total amount of metals) of 2:1 ligand–metal complexes, 1:1 complexes, and free metals for noncooperative metal–ligand complexation $\Delta E_1 = \Delta E_2 = 8kT$. Computer simulation data are shown as symbols, whereas predictions of the analytical model are solid curves.

ligand–metal complexes in rings is more than 10 times smaller than in chains and the overall degree of association is practically coincident with that in chains. Since the degree of association is directly related to the molecular weight (as discussed below), the weight fraction of rings is also very small. We note that apart from the case of strong dilution (discussed below), the fraction of rings in metallosupramolecular polymers is noticeably smaller than that produced in donor–acceptor-type self-association of linear oligomers.²⁸ The main reason for this is a higher entropic loss (rigidity) of 2:1 ligand–metal complexes compared to donor–acceptor-type association. Therefore metal–ligand association results mainly in chain formation and below we will omit showing the ring fraction (except for dilution study).

The degree of association increases with an increase in metal fraction, reaching the maximum at the stoichiometric composition (one metal per two ligands). At a higher metal content the degree of association decreases faster than its increase rate in the oligomer-excess region. The general reason for the decrease in the degree of association away from stoichiometric composition is a mismatch in number of metals and ligands. However, the asymmetry of the decrease in the metal-rich compared to the metal-poor region requires additional consideration.

To gain insight on the process of metal–ligand complex formation, we have also calculated the fraction of 1:1 ligand–metal complexes with respect to the total metal ions amount, m_1 . Experimentally the fraction of 2:1 complexes, m_2 , and free ligands, m_0 , can be estimated from NMR measurements.^{13,16,20,21,23} Knowing these values, the fraction of 1:1 complexes can be evaluated as well ($m_1 = 1 - m_0 - m_2$). The fractions of free metals and 1:1 and 2:1 ligand–metal complexes (also calculated with respect to the total number of metal ions) are compared in Figure 3 as a function of the metal content, $\mathcal{N}_m / \mathcal{N}_0$. As is seen, the fraction of 2:1 complexes (m_2) is maximal in the metal-poor region and it strongly decreases above the stoichiometric composition. The reason for this decrease is an increase in 1:1 ligand–metal complex formation, which implies effective depolymerization of metallosupramolecular polymers. Having the same enthalpic gain for the metal association with the first and second ligand ($\Delta E_1 = \Delta E_2$) favors the 1:1 complex formation because of the considerably larger entropic penalty for the 2:1 complex. As a result of the strong competition between 1:1 and 2:1 ligand–metal complexes, the average

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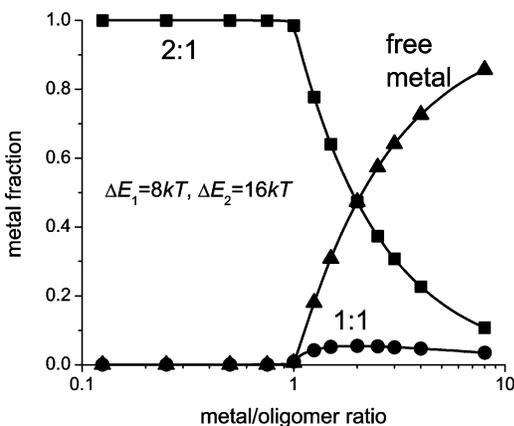


Figure 4. Composition dependence of the average fraction (with respect to total amount of metals) of 2:1 ligand–metal complexes, 1:1 complexes, and free metals for cooperative metal–ligand complexation $\Delta E_1 = 8kT$, $\Delta E_2 = 16kT$. Computer simulation data are shown as symbols, whereas predictions of the analytical model are solid curves.

degree of association (Figure 2) and therefore the molecular weight of the self-assembled polymers remains high only in a relatively narrow region near the stoichiometric point (one metal per two ligands).

Cooperative Complexation. Since formation of 1:1 ligand–metal complexes is the main reason for the rapid decrease in the molecular weight of metallosupramolecular polymers for metal-rich compositions, one of the ways to increase the molecular weight is to make 2:1 complexes more thermodynamically favorable. Taking into account that 2:1 ligand–metal complexes are intrinsically more rigid (accompanied by a larger entropic loss) than 1:1 complexes, the former must have a larger enthalpic drive to become more favorable in the metal-rich regime. It is experimentally known that the association constants for 1:1 and 2:1 complexes may be quite different depending on the nature of the metal ions³¹ (as well as the conditions of complex formation). Therefore, on the basis of the above arguments, metals with a more favorable association constant or strength of the second metal–ligand bond ΔE_2 will form a smaller fraction of 1:1 complexes (m_1) and produce higher molecular weight polymers as a result. We have doubled the enthalpic gain for the second ligand association to a metal ($\Delta E_2 = 16kT$) while keeping $\Delta E_1 = 8kT$ and calculated the fraction of free metals and 1:1 and 2:1 complexes (with respect to initial amount of metal ions), as shown in Figure 4. By comparing the results for noncooperative ($\Delta E_1 = \Delta E_2 = 8kT$, Figure 3) and cooperative ($\Delta E_1 = 8kT$, $\Delta E_2 = 16kT$, Figure 4) complexes, one can see that indeed the cooperative complexation results in a considerable decrease in the amount of 1:1 complexes and enhancement of 2:1 complexes.

Figure 5 shows the total degree of association and average molecular weight (calculated in units of oligomer weight, see inset) for three metal ions with the same enthalpy gain for 1:1 complexes $\Delta E_1 = 8kT$ but different cooperativity: $\Delta E_2 = 8kT$, $12kT$, and $16kT$. The larger the energetic drive for the second metal–ligand association compared to the first one, (i.e., the larger cooperativity of association, $\Delta E_2 - \Delta E_1$) the larger the degree of association in the metal-rich area and the slower its decrease with an increase of metal content. The molecular

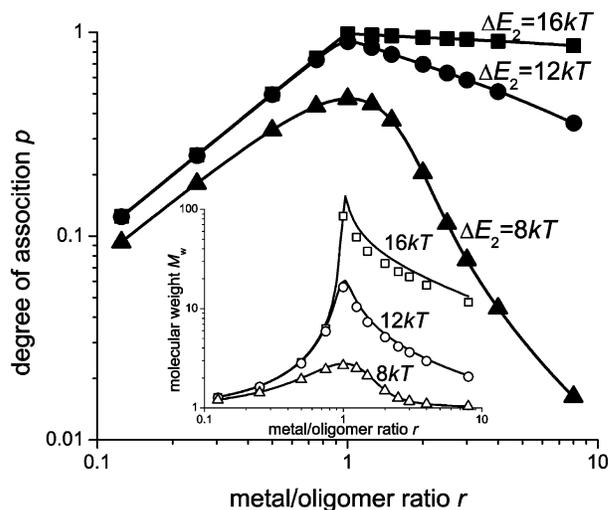


Figure 5. Composition dependence of the average degree of association (fraction of 2:1 complexes) for metals with different degrees of cooperativity $\Delta E_1 = 8kT$, $\Delta E_2 = 8kT$, $12kT$, and $16kT$. (Inset) Corresponding weight-average molecular weights (in units of oligomer weight). Computer simulation data are shown as symbols, whereas predictions of the analytical model are solid curves.

weights of the complexes follow the same trend: the molecular weight achieved at the stoichiometric composition for the metal with $\Delta E_2 = 16kT$ is nearly 10 times larger than that for the metal with $\Delta E_2 = 12kT$ and 100 times larger than for a noncooperative metal $\Delta E_2 = \Delta E_1 = 8kT$ (see the inset of Figure 5). Therefore, if one wants to achieve high molecular weight polymers by metal–ligand complexation, the metal should be chosen with a high degree of cooperativity, $\Delta E_2 - \Delta E_1$ (i.e., higher strength of the second metal–ligand bond compared with the first). Still, the molecular weight rapidly decreases away from the stoichiometric composition even for metals with a high degree of cooperativity. What are the factors defining the decrease of molecular weight in the metal-rich area and what can be done to increase the range of compositions where high molecular weight metallosupramolecular polymers can be achieved?

Analytical Model. To understand the complex formation in more detail, we have applied a simple analytical model based on chemical equilibrium. By an approach similar to that described in ref 28, the fraction of 1:1 (m_1) and 2:1 ligand–metal complexes (m_2) can be calculated as a solution of the following two equations:

$$\tilde{K}_1(2\mathcal{N}_0 - \mathcal{N}_m m_1 - 2\mathcal{N}_m m_2)\mathcal{N}_m(1 - m_1 - m_2)\frac{v}{V} = \mathcal{N}_m m_1 \quad (2)$$

$$\tilde{K}_2(2\mathcal{N}_0 - \mathcal{N}_m m_1 - 2\mathcal{N}_m m_2)\mathcal{N}_m m_1 \frac{v}{V} = \mathcal{N}_m m_2 \quad (3)$$

where $\tilde{K}_1 = \exp(\Delta E_1/kT - \Delta S_1)$ and $\tilde{K}_2 = \exp(\Delta E_2/kT - \Delta S_2)$ are analogous with the equilibrium constants for 1:1 and 2:1 ligand–metal complexes. ΔS_1 and ΔS_2 are the entropy losses for formation of the corresponding complexes. V is the total volume of the system and v is the reference volume (in the BFM the reference volume reflects the number of available sites for nearest neighbors, $v \approx 108a^3$).

By solving the system of equations numerically (for details see Supporting Information), one can predict the fraction of 1:1 and 2:1 complexes and the total degree of association $p =$

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$m_2 \mathcal{N}_m^c / \mathcal{N}_0^c$ as a function of metal content and concentration (as well as temperature). The results of the analytical model are shown in Figures 3–5 as solid curves. We note that the best fit of all the curves resulted in the same value for the entropic loss ($\Delta S_1 = 1.525 \pm 0.03$ and $\Delta S_2 = 5.21 \pm 0.03$, which were used as fitting parameters). This confirms the self-consistency of the analytical approach: since the rigidity factor in MC simulation was independent of the enthalpy gain of complex formation, the fitting should produce the same values for ΔS_1 and ΔS_2 in all cases, as it does. As is seen, in all cases the agreement between the simulation results and analytical predictions is very good, signifying that the simple analytical model represents the complexation correctly. This model can be used (as described in Supporting Information) for analysis of experimental data or for prediction of the degree of association (and estimation of molecular weight, as discussed below) for any metal–ligand complexes. To estimate the weight-average molecular weight shown in the inset of Figure 5, we applied the simple relation known in condensation polymerization theory,²⁵ $M_w = (1 + p)/(1 - p)$ with $p = m_2 \mathcal{N}_m^c / \mathcal{N}_0^c$, calculated from eqs 2–3. We note that this expression is only an approximation since it does not account for ring formation or rigidity of complexation (which may change the average molecular weight).

Analysis of our MC data and predictions of the analytical model for the metals with different degrees of cooperativity demonstrates that the strong decrease in the molecular weight at metal contents just above the stoichiometric composition is due to the dissociation of 2:1 complexes to yield 1:1 ligand–metal complexes. Even if the maximal fraction of 1:1 complexes is small (as in Figure 4), it still decreases the overall degree of association (i.e., fraction of 2:1 complexes) and results in a considerable drop in the molecular weight. To avoid this problem, the maximum in the fraction of 1:1 complexes m_1 should occur at the same (or very close) composition as the maximum of the degree of association p (and hence the molecular weight). Since the analytical model describes the MC data pretty well, we could calculate numerically the compositions corresponding to the maximum in m_1 and p (as functions of ΔE_1 and ΔE_2) and obtain the critical curve when the two compositions coincide (Figure 6). Due to the complexity of these calculations, an analytical expression for this curve is not readily available. However, there are two simple asymptotic limits. At low ΔE_2 (strength for the second ligand–metal bond) the curve can be approximated as $\Delta E_1 = 11.2kT - \Delta E_2$ whereas at high ΔE_2 it approaches constant value: $\Delta E_1 \approx 3.775kT$. Therefore, if

$$\Delta E_1 \lesssim 11.2kT - \Delta E_2 \text{ or } \Delta E_1 \lesssim 3.775kT \quad (4)$$

the maximum in 1:1 complex formation will occur at lower (or comparable) metal content as the maximum in the degree of association (and molecular weight). In such a case, further increase in metal content will not lead to ligand redistribution between 2:1 and 1:1 complexes. However, the condition of eq 4 does not guarantee a high absolute value of the molecular weight. As we discussed above, the higher the cooperativity of complexation (larger $\Delta E_2 - \Delta E_1$), the larger the fraction of 2:1 complexes and therefore the higher the molecular weight. More detailed calculations show that the fraction of 2:1 complexes (m_2) exceeds the maximum amount of 1:1 complexes (m_1) when

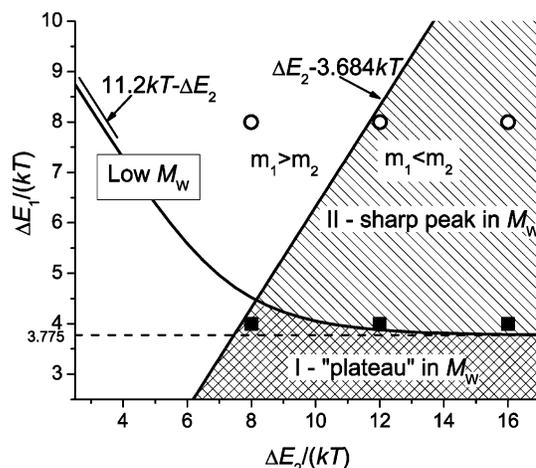


Figure 6. Analytical diagram for the ΔE_1 and ΔE_2 values (for $\Delta S_1 \approx 1.525$ and $\Delta S_2 \approx 5.21$) that define the conditions when (I) the molecular weight of supramolecular polymers is high and exhibit a plateau (gradual decrease) in the metal-rich regime (cross-hatched region), (II) the molecular weight can be high but only in a very limited range of compositions around the stoichiometric point (equal fraction of metal to oligomers) (titled line, hatched region). In the rest of the diagram space, mono complexes (1:1) dominate 2:1 complexes and the molecular weight is low, having a sharp maximum at the stoichiometric composition. MC data depicted in Figures 5 and 7 are shown as open and solid symbols, respectively.

$$\frac{\Delta E_2 - \Delta E_1}{kT} \geq \Delta S_2 - \Delta S_1 \approx 3.684 \quad (5)$$

To ensure under thermodynamic equilibrium both the high absolute value of the molecular weight and its slow decrease with an increase of metal content (in the metal-rich area), conditions of both eqs 4 and 5 should be satisfied (shown as cross-hatched area in Figure 6). In such a case 2:1 complex formation dominates and there is no ligand redistribution between 2:1 and 1:1 complexes since the maximum in 1:1 ligand–metal complexes occurs at lower metal content than the maximum in the degree of association p . As a result, a high molecular weight of supramolecular polymers can be achieved and maintained even when the metal content exceeds the stoichiometric composition (i.e., plateau-like behavior). Therefore, to obtain high molecular weight complexes with plateau-like behavior of the molecular weight in the metal-rich area, one should choose metal–ligand complexes with small enthalpy gain for the 1:1 complex formation $\Delta E_1 \lesssim 3.775kT$ (eq 4) and large cooperativity, $\Delta E_2 - \Delta E_1 \gtrsim 3.684kT$ (eq 5). Examples of such behavior will be considered below. We note that among conditions of eq 4 only the second one ($\Delta E_1 \lesssim 3.775kT$) is important when eq 5 is satisfied. Moreover, the upper limit on ΔE_1 value ($\Delta E_1^{\text{cr}} \approx 3.775kT$) can be extended to somewhat higher values since for metals that exhibit high cooperativity the maximum in 1:1 complexes is rather shallow (and small in absolute values as shown in Figure 4).

The area where the condition of eq 5 is satisfied but the condition of eq 4 is violated is shown in Figure 6 as a hatched region. In this region a high molecular weight of supramolecular polymers can be achieved but only in a narrow composition range near the stoichiometric point. Examples of such behavior we have been considered above (Figure 5) and indicated in Figure 6 as open symbols. In all cases $\Delta E_1 > 3.775kT$ and there is a ligand redistribution between 2:1 and 1:1 complexes leading to a sharp peak in molecular weight near the stoichiometric condition.

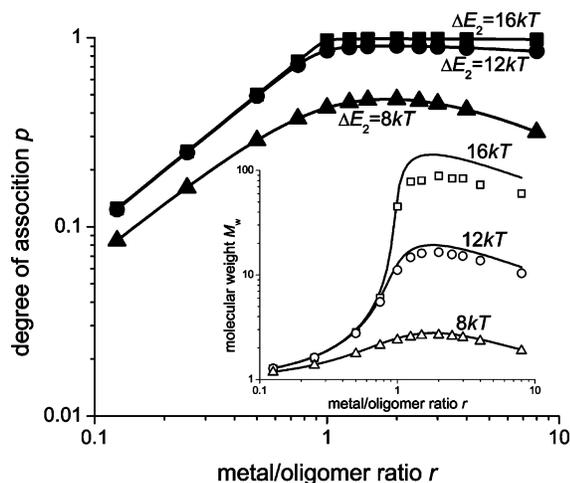


Figure 7. Composition dependence of the average degree of association (fraction of 2:1 complexes) for the metals with smaller enthalpy for 1:1 complexes, $\Delta E_1 = 4kT$ (compared to Figure 5) and different degree of cooperativity $\Delta E_2 = 8kT$, $12kT$, and $16kT$. (Inset) Corresponding weight-average molecular weights (in units of oligomer weight). Computer simulation data are shown as symbols, whereas predictions of the analytical model are solid curves.

Comparison of Theoretical Predictions with MC Data and Experimental Results.

The predictions of our analytical model regarding the conditions when high molecular weight polymers can be formed over a large composition range have been tested in MC simulations. We have decreased the enthalpy for the 1:1 complex formation to $\Delta E_1 = 4kT$ and used the same enthalpy for the second ligand–metal association, ΔE_2 , as in Figure 5 (i.e., $\Delta E_2 = 8kT$, $12kT$, and $16kT$). This corresponds to the conditions (inside or slightly outside the cross-hatched area as shown by solid symbols in Figure 6) when a gradual decrease in molecular weight in the metal-rich area is expected. And indeed, as shown in Figure 7, the average degree of association and the weight-average molecular weight (in units of oligomer weight) in all three cases decrease rather slowly with an increase in metal content in the metal-rich area. The behavior of the weight-average molecular weight is in striking contrast to that observed in Figure 5 (for $\Delta E_1 = 8kT$). Upon comparing maximum values of the molecular weight shown in Figures 5 and 7, one can notice that it depends mainly on ΔE_2 (strength of the second metal–ligand bond). At the same time the rate of molecular weight decrease in the metal-rich area is determined by the value of ΔE_1 (enthalpic gain for 1:1 complex formation). Since in the case of Figure 5 ΔE_1 is larger than the critical value (shown in Figure 6), the molecular weight rapidly decreases with metal content (in the metal-rich area). On the other hand, for $\Delta E_1 = 4kT$ (shown in Figure 7) $\Delta E_1 \lesssim \Delta E_1^{ct}$ and we observe a gradual decrease in molecular weight. Therefore, to obtain a high molecular weight supramolecular polymer it is desirable to have high values of ΔE_2 and to maintain a high molecular weight over a wide range of compositions (in the metal-rich area) ΔE_1 should be small ($\Delta E_1 \lesssim \Delta E_1^{ct} \approx 3.775kT$). In other words, the metal ion should have high cooperativity ($\Delta E_2 - \Delta E_1$) and the enthalpic gain for 1:1 complexes (ΔE_1) should be small.

Experimental measurement of the molecular weight is not always possible for truly thermodynamically equilibrated complexes because of the dissociation of complexes in the process of the measurements.^{3,16,20} Often viscosity measurements are

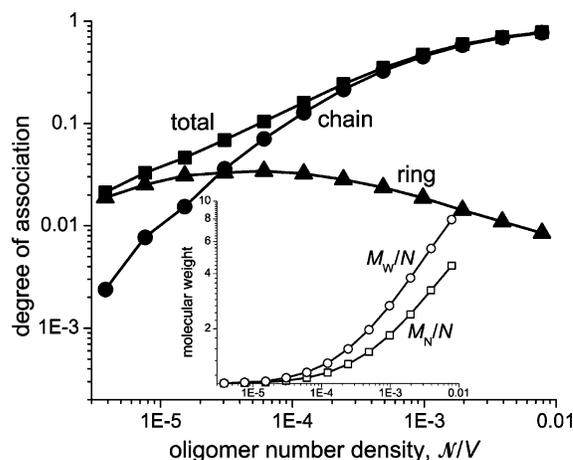


Figure 8. Average degree of association (fraction of 2:1 complexes) for chains, rings, and in total as a function of initial oligomer density for stoichiometric (one metal per two ligands) noncooperative metal–ligand complexation $\Delta E_1 = \Delta E_2 = 8kT$. (Inset) Corresponding weight-average and number-average weights calculated in units of oligomer weight.

used to estimate the average molecular weight,^{20,21} but it is worthwhile to note that such estimations can be somewhat misleading. Upon dilution of the supramolecular polymers, their average degree of association will decrease (as discussed in the next section) and the measured viscosity will change as a result of both dilution and decomplexation of the polymers.²³ At the same time, viscosity measurements performed at the constant polymer concentration but with changing metal content should provide a good measure of the degree of association and the molecular weight. Recent measurements of the viscosity of metallosupramolecular polymers formed by telechelic bis(2',2':6',2''-terpyrid-4'-yl)poly(ethylene oxide)₁₇₉ (in methanol) upon addition of different metal ions [cadmium(II), copper(II), cobalt(II), nickel(II), and iron(II)] show an overall behavior very similar to that depicted in Figures 5 and 7.²⁰ Some of the metal ions [iron(II) or nickel(II)] produced supramolecular polymers of high viscosity, which slowly decreases with an increase in the metal content above the stoichiometric composition. The viscosity of supramolecular polymers formed with the participation of other metals [such as cobalt(II) or copper(II)] was noticeably smaller and changed much more quickly away from the stoichiometric composition. Taking into account that the difference in association constants for bis and mono complexes of Fe(II) exceeds that for Co(II)³¹ and the association constant for mono complex formation is smaller for Fe(II) [compared to Co(II)], the observed results for these metals agree well with our predictions. However, for Ni(II) the difference in association constants between bis and mono complexes is rather small, plus the association constant for the mono complex is higher than for Fe(II) or Co(II)³¹ and still it shows a very weak composition dependence in the metal-rich area. The possible explanation for this discrepancy may be in the interactions of the metal with solvent, the larger difference in the entropy of bis and mono complexes for Ni(II) compared to other metals or it can be the result of kinetic effects, which are not considered in the present paper.

Concentration Dependence. Besides the influence of composition considered above and the nature of metal ions, the complex formation depends also on concentration, (oligomer–solvent, ligand–solvent) volume interactions, electrostatic interactions, and temperature. Whereas the effect of the latter three will be a subject of our future work, the effect of dilution of a

good solvent solution of the metallocupramolecular polymer considered in Figures 2 and 3 (noncooperative case) on its degree of association and average molecular weight is shown in Figure 8. We note that the metal/ligand ratio was kept constant. As is seen, dilution leads to consistent decrease in the overall degree of association and in the fraction of 2:1 complexes forming chains. At the same time the fraction of 2:1 complexes in rings gradually increases upon dilution until it exceeds that in chains and then fraction of rings starts to decline as well. It is worthwhile to note that while at high concentration the contribution of rings is practically negligible, at low concentration rings play a dominant role and cannot be neglected. The weight-average and number-average molecular weights (in units of oligomer weight) strongly decrease upon dilution. The rate of the decrease changes from linear (in the chain-dominated regime) to nonlinear (in the ring-dominated regime). As a result, the viscosity of thermodynamically equilibrated complexes is expected to decrease much more quickly upon dilution than for kinetically frozen complexes. Decomplexation and formation of rings upon strong dilution of supramolecular polymers formed by *p*-phenyleneethynylene-bridged bis[9-(*p*-anisyl)-*o*-phenanthroline] ligand monomers and [Cu(CH₃CN)₄]PF₆ or AgBF₄ in slightly moist acetone has been recently reported (on the basis of viscometric and ¹H NMR measurements).²³ They found that the equilibrium complexation (or decomplexation) occurs only in coordinating media (such as slightly moist acetone), whereas in noncoordinating solvents (such as dry TCE) the complexes are kinetically frozen and dissociation does not occur upon dilution.

4. Conclusions

Applying a combined MC simulation and analytical approach (based on chemical equilibrium), we have studied thermodynamically equilibrated metal–ligand complexation (with up to two ligands per metal) leading to formation of linear or ringlike supramolecular polymers. We found that in general ring fraction remains rather low apart from the case of strong dilution. We have studied the influence of the metal content and enthalpy of complexation on the degree of association and average molecular weight. We found that in most of the cases the molecular weight reaches its maximum at the stoichiometric composition and rapidly decreases with an increase (or decrease) in metal content. Analyzing the distribution of metals between the 1:1 and 2:1 ligand–metal complexes, we found that the reason for the decrease in molecular weight is the enhancement of 1:1 complex formation for metal-rich compositions. Applying our analytical model, we obtained the criterion for achieving high molecular weight polymers in the metal-excess composition range: the metal/ligand pair should have a small enthalpy gain for the 1:1

complex formation ($|\Delta E_1| \lesssim 3.775kT$) and a large cooperativity ($|\Delta E_2 - \Delta E_1| \gtrsim 3.684kT$), that is, a large enthalpy gain for the second ligand–metal bond. This criterion can be used to guide the selection of appropriate metal–ligand pairs.

The current state of experimental research does not allow direct numerical comparison with our analytical predictions, mainly due to the difficulties in determining molecular weights.^{3,16,20} However, qualitative comparison with recent viscosity data for metallocupramolecular polymers measured at constant concentration as a function of metal content²⁰ is encouraging. Further experimental research involving more metal ions and ligand types will allow our predictions to be tested quantitatively. We also plan to perform molecular dynamic simulations to help estimate the enthalpy and entropy of complexation for different metal/ligand pairs in various solvents in order to make comparison with experimental data more straightforward.

We have also studied the effect of dilution of stoichiometric metal–ligand complexes on molecular weight and chain-ring equilibrium of supramolecular polymers. We found that dilution leads to a decrease of the average degree of association (decrease in 2:1 ligand–metal complexes) and enhancement of ring formation. As a result the molecular weight will also decrease upon dilution. Decomplexation and formation of rings upon strong dilution of supramolecular polymers has been reported recently (on the basis of viscometric and ¹H NMR measurements).²³ Further experimental research may allow direct quantitative comparison with our theoretical predictions.

Understanding of the basic principles of metallocupramolecular self-assembly may stimulate further experimental research directed toward formulation of the novel class of responsive materials that combine the properties of traditional synthetic polymers with the versatility of biomolecules.⁸ As in the biological world, the components of modern supramolecular polymers contain the information required for their assembly into a well-defined supramolecular entity through the operation of specific recognition algorithms. Understanding, inducing, and directing these self-assembly processes are the key to future design of these novel materials.⁸

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Supporting Information Available: Solution of the equations of chemical equilibrium (eqs 2 and 3) (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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