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Density functional complexation study of metal ions with poly(carboxylic acid) ligands. Part 2. Poly(acrylic acid-*co*-maleic acid), poly(methyl vinyl ether-*co*-maleic acid), and poly(epoxy succinic acid)

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Abstract

We have studied metal ion complexation with poly(carboxylic acid) ligands using density functional methods and a continuum-solvation model (COSMO). Geometry optimisations have been carried out for metal complexes of poly(acrylic acid-*co*-maleic acid), poly(methyl vinyl ether-*co*-maleic acid), and poly(epoxy succinic acid) oligomers. The complexation energies for Mg^{2+}, Ca^{2+}, Mn^{2+}, and Fe^{3+} have been calculated and they have been corrected with previously determined metal specific correction parameters. The most effective ligand for all the metal ions was found to be poly(epoxy succinic acid). With Ca^{2+}, poly(epoxy succinic acid) was found to form 6-coordinated complex with three metal-coordinating carboxylate oxygen, two ether oxygens, and one hydroxyl oxygen atom. All the other metals favoured 5-coordinated complexation geometry with four metal-coordinating carboxyl oxygens and one ether oxygen atom.

Keywords: Ab initio; Complexation; Metal ions

1. Introduction

One of the most interesting and common chemical reactions is complexation, which occurs both in nature and in human body. Complexation reactions are widely used also in different industrial processes in order to inactivate or remove metal ions. In agricultural applications, iron is added in soils in a stable complexes to prevent iron deficiency in plants. In the pulp bleaching process, the most harmful metal ions are manganese and iron, which participate in the decomposition of hydrogen peroxide and peracids. In addition to these transition metals, pulp contains also magnesium and calcium. The former has been found to be beneficial to the bleaching process, the latter is inactive, and thus, their complexation only consumes the complexating agent [1]. The well-known and efficient nitrogen-containing chelators, e.g. EDTA (ethylene diamine tetraacetic acid) and DTPA (diethylenetriamine pentaacetic acid), display low biodegradability and they mobilise heavy metals from sediments in natural waters [2]. Thus, it is important to develop and study more environmentally friendly complexing agents. One interesting group of these includes (nitrogen free) polycarboxylic acids, e.g. poly(acrylic acid) and its derivatives.

Polyelectrolytes and their complexation properties have been widely studied by experimental methods [3]. Among the most studied functional groups are carboxylic acid groups [4,5]. Also, ligands including hydroxyl groups and ether oxygen atoms have been studied carefully. In this present study, we have chosen to study metal complexes of three different polymers, two of them being copolymers of commonly known polycarboxylic acid, poly(acrylic acid-*co*-maleic acid), P(AA-MA), and poly(methyl vinyl ether-*co*-maleic acid), P(MVE-MA). The third polymer in this study was chosen to be poly(epoxy succinic acid), PESA.

In our first study of metal complexation [6] we focused on metal ions with non-polymeric (amino)polycarboxylic acid ligands using density functional theory (DFT) with the COSMO solvation model and Car-Parrinello ab initio

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molecular dynamics. As a result, a fast, accurate, and straightforward (DFT-COSMO) computational method for evaluating the performance of complexing agents was developed. The method was further applied to homopolymeric ligands, poly(acrylic acid) and poly(α-hydroxy acrylic acid) [7] and the results (obtained binding degrees and complexation geometries) were promising compared to the available experimental data. The aim of this study was to apply the same computational method for copolymer systems. The complexation of Mg^{2+}, Ca^{2+}, Mn^{2+}, and Fe^{3+} with poly(acrylic acid-*co*-maleic acid), poly(methyl vinyl ether-*co*-maleic acid), and poly(epoxy succinic acid) oligomers was studied.

It is clear that modelling of copolymers and their metal complexes with ab initio method is more complicated than the case of homopolymers [7]. However, as the monomer units and functional groups of studied copolymers are similar both to previously studied oligomers of poly(acrylic acid) and poly(α-hydroxy acrylic acid), and well-known (amino)poly carboxylic acid ligands studied by Sillanpää et al. [6], we find it both interesting and relevant to apply our method with other type oligomer ligands. All the polymers and their complexation behaviour will be further studied in future with the means of molecular dynamics.

2. Computational details

All geometry optimisations have been performed using the program TURBOMOLE [8]. We have employed the TZVP basis set for all atoms and the BP86-functional [9] throughout the study. The RI-approximation [10] has been used to speed up the calculations. All geometries have been optimized using the COSMO-solvation model [11]. The determination of the COSMO-radii for metal ions is described in detail in our previous articles [6,7], otherwise the default options in the program TURBOMOLE have been used. For the transition metal complexes we have employed the spin unrestricted formalism and for the earth alkaline metal complexes the spin restricted formalism. The Fe^{3+} and Mn^{2+} complexes have been taken to be in the high spin state. In general, we have begun with Mg^{2+} complexes, and then used the optimised geometry of Mg^{2+} complex as a starting configuration for other metals.

3. Results

In this section, we will first describe the results obtained for the free ligands in (computational) water. Then, we will present the results for metal complexes of poly(acrylic acid-*co*-maleic acid), poly(methyl vinyl ether-*co*-maleic acid), and poly(epoxy succinic acid) and in the end of this section, we will make some comparisons pertaining to the complexation properties of these three ligands and the previously studied oligomer ligands [7]. General considerations on the applicability of this method are discussed in Section 4. Monomer units of studied ligands are shown in Fig. 1.

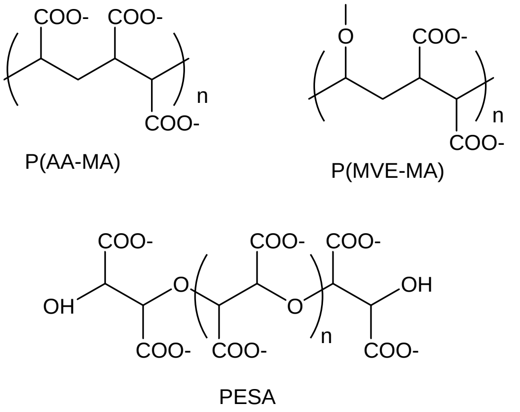

Fig. 1. Monomer units of studied ligands. Hydrogen atoms are excluded for the clarity. For P(AA-MA), we have studied situation where *n* is 1 and 2, and for P(MVE-MA), *n* has been chosen to be 2. For PESA-ligand, *n* was chosen to be 1.

3.1. Free oligomers

In order to find the minimum energy structures for oligomer ligands, we optimised 3–5 structures for each oligomer at BP86/TZVP level of theory using COSMO-solvation model. Different stereochemical configurations were considered and molecular mechanics (MM2) was used in generating the starting configurations. As the oligomers in this study are mainly composed of deprotonated carboxylic acid groups attached to carbon backbone, possible stereochemical variation include basically the orientation of the sequential carboxylate groups and thus, we are quite convinced that the found minimum energy structures represent global minima for oligomers at the appropriate level.

Optimised minimum energy structures for free oligomers are shown in Fig. 2 together with their COSMO-corrected total energies (in au).

3.2. Metal complexes

We have performed geometry optimisations for metal complexes of P(AA-MA), P(MVE-MA), and PESA oligomers to obtain the minimum energy complex structures. Different stereochemical configurations for the ligands have been taken into account. All different bonding configurations were separately optimised for Mg^{2+}, Ca^{2+}, Mn^{2+} and Fe^{3+} metal ions. Complexation energies were determined according to Eq. (1):

$$\begin{aligned}\Delta E_{\mathrm{CO}} &= \Delta E_{\mathrm{CSM}} \\ &= E_{\mathrm{CSM}}(\mathrm{ML}^{n-m}) + 6E_{\mathrm{CSM}}(\mathrm{H_2O}) - E_{\mathrm{CSM}}(\mathrm{L}^{-m}) \\ &\quad - E_{\mathrm{CSM}}\left(\mathrm{M(H_2O)}_6^{n}\right) \qquad (1)\end{aligned}$$

where $E_{\mathrm{CSM}}(X)$ is the COSMO-corrected total energy of species (X). M and L refer to metal and ligand, respectively. n is the charge of the metal and m the charge of the ligand. Since there are no experimental solvation free energy data for the metal–oligomer complexes available, and since based on

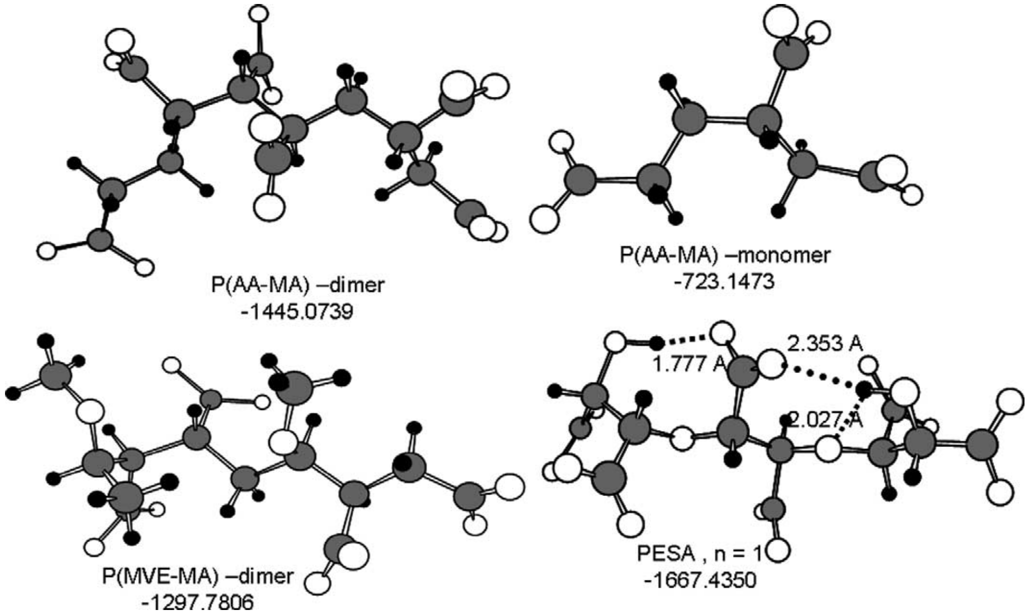

Fig. 2. Optimised geometries for free ligands together with their COSMO-corrected total energies (in a.u.). White spheres depict oxygen atoms, black spheres hydrogens, and dark gray carbon atoms. Hydrogen bonds are shown with dotted lines together with their length (in Ångströms).

previous similar calculations we expect large deviations from experimental complexation energies, ΔE_{CO} were corrected with the metal specific correction parameters, $\tilde{G}_{\mathrm{ML}_i}$, determined previously for the same method applied to (amino) polycarboxylic acid ligands, including, e.g. EDTA (ethylenediamine tetraacetic acid) and DTPA (diethylenetriamine pentaacetic acid). These parameters were determined by fitting the complexation energies obtained by the DFT/COSMO-approach to reproduce the experimental data. The corrected complexation energies are then determined according to Eq. (2):

$$\Delta G_{\mathrm{C}}(\mathrm{M}_i, \mathrm{L}_j) = \Delta E_{\mathrm{CO}}(\mathrm{M}_i, \mathrm{L}_j) + \tilde{G}_{\mathrm{ML}_i} \qquad (2)$$

The correction parameters are shown in Table 1 (values taken from Ref. [6]). Even if the use of only metal-dependent correction is a very crude approximation and the correction has been derived from non-polymeric ligands these parameters seem to work quite well. We have compared our results to all experimental results [13] we have found and qualitatively our concept has been able to reproduce basically all experimentally observed trends. We like to conclude that even our approach is crude the relative energies (of this type of ligands studied here) are qualitatively correct and the computed geometries are rather accurate.

3.2.1. Metal complexes of poly(acrylic acid-co-maleic acid)

In order to study complexation behaviour of poly(acrylic acid-*co*-maleic acid) we optimised metal complexes of Mg^{2+}, Ca^{2+}, Mn^{2+}, and Fe^{3+} both with one ligand and two ligands. One ligand was, simply for computational reasons, chosen to be P(AA-MA)-dimer with two monomers from both acrylic acid and maleic acid. Two ligands were, respectively, chosen to be monomer units of P(AA-MA). All carboxylic acid groups were assumed to be deprotonated. Different stereochemical configurations and coordination modes were considered.

As expected, the most favourable coordination numbers of P(AA-MA)-metal complexes were found to be low (less than six, which is the most common coordination number for all four metal ions in aqueous environment). In order to further study energetics and geometries of metal complexes of P(AA-MA), we optimised two (most favourable) geometries for Mg^{2+} with explicit water molecules. The total coordination number of six was assumed. As the used conductor-like approach for the solvent has been shown to be more reliable for the negatively charged species with respect to the dielectric continuum models [14], we did not find necessary to add explicit solvent molecules around the whole complex.

Optimised 3- and 4-coordinated metal complexes of P(AA-MA), together with their uncorrected and corrected complexation energies (in kJ mol^{-1})are shown in Table 2. All the structures for Mg^{2+}-complexes are shown in Fig. 3. Table 2 and Fig. 3 include the geometries optimised with explicit water molecules.

As shown in Table 2, corrected complexation energies for metal ions with P(AA-MA)-dimer ligand (geometries **3a***, **4a***, and **4b***, respectively) are positive. Comparison of the corrected complexation energies indicates that the P(AA-MA)-dimer is clearly the most effective binder for the Fe^{3+} ion and least effective for alkaline earth metal ions Ca^{2+} and Mg^{2+}. The difference between transition metal ions with different oxidation state (Fe^{3+} and Mn^{2+}, respectively) is 23 kJ mol^{-1}, which can be considered noteworthy in

Table 1
Correction parameters for metal ions (in kJ mol^{-1}), see Ref. [6] for details

Metal ion	Mg^{2+}	Ca^{2+}	Mn^{2+}	Fe^{3+}
$\tilde{G}_{\mathrm{ML}_i}$	91	77	115	284

Table 2
Metal complexes of P(AA-MA) dimer ligand and two P(AA-MA) monomer ligands, their uncorrected and corrected complexation energies (in kJ mol^{-1})

Metal	Coord.	ΔE_{co} (kJ mol^{-1})	ΔG_{c} (kJ mol^{-1})
Mg^{2+}	3a[a]	−55	36
Ca^{2+}	3a[a]	−43	34
Mn^{2+}	3a[a]	−88	27
Fe^{3+}	3a[a]	−269	15
Mg^{2+}	4a[a]	−30	61
Ca^{2+}	4a[a]	−17	60
Mn^{2+}	4a[a]	−70	45
Fe^{3+}	4a[a]	−272	12
Mg^{2+}	4b[a]	−37	54
Ca^{2+}	4b[a]	−21	56
Mn^{2+}	4b[a]	−76	39
Fe^{3+}	4b[a]	−280	4
Mg^{2+}	4c[b]	−66	25
Ca^{2+}	4c[b]	−59	18
Mn^{2+}	4c[b]	−117	−2
Fe^{3+}	4c[b]	−297	−13
Mg^{2+}	4d[c]	−44	47
Mg^{2+}	4e[d]	−76	15

See Fig. 3 for geometries.

[a] One ligand.

[b] Two ligands.

[c] One ligand with explicit water molecules.

[d] Two ligands with explicit water molecules.

comparison with the differences between divalent metal ions (between Mn^{2+} and Ca^{2+} 7 kJ mol^{-1}, and between Ca^{2+} and Mg^{2+}2 kJ mol^{-1}, respectively). For Fe^{3+}, the most favourable complexation geometry with P(AA-MA)-dimer ligand was found to be 4-coordinated (**4b***) while all the other metal ions favoured 3-coordinated structure **3a***. However, one should keep in mind that Fe^{3+} is the single studied trivalent metal ion and thus, it is difficult to estimate how much the charge of the ion has influence in this case.

With two P(AA-MA) monomer ligands, all the metal ions favoured coordination number of four (structure **4c****). In the lowest energy structure all the metal-bonding carboxylate oxygen atoms are from maleic acid units of the copolymer. In general, complexation energies of these complexes are lower than with one ligand. This was also observed in our study with metal complexes of poly(acrylic acid) [7]. However, the method was developed for metal complexes with one ligand and, thus, the results with two ligands must be viewed with certain critisism.

As seen in Table 2 and Fig. 3, the inclusion of explicit water molecules in the first solvation shell of the Mg^{2+} ion improve slightly the complexation energies but does not change noticeably the complexation geometries previously optimised without them. For example, the distances between metal ion and metal-coordinating carboxylate oxygen atoms increase approximately 2% when the explicit water molecules are added in the structure **4b***. The O_{carb}–M–O_{carb}-angles, on the other hand, decrease 2–5%. Explicit water molecules prefer to form hydrogen bonds with carboxylate oxygen atoms of the ligand(s). This observation was also made in our study [6], where the cluster-continuum model was applied for $[\mathrm{CaISA}]^{2-}$-complexes.

3.2.2. Metal complexes of P(MVE-MA)

In order to study complexation behaviour of P(MVE-MA) we optimised metal complexes of Mg^{2+}, Ca^{2+}, Mn^{2+}, and Fe^{3+} with P(MVE-MA)-dimer. All carboxylic acid groups were assumed to be deprotonated. Different stereochemical configurations and coordination modes were considered. A combined cluster-continuum approach was applied for one 4-coordinated complex for all metal ions. Table 3 shows the obtained complexation energies for different coordination modes (Fig. 4 for geometries).

For all metal ions, the most favourable coordination mode was structure **4a** with three metal-binding carboxylate oxygen atoms and one metal-binding ether oxygen atom. Comparison of the corrected complexation energies indicates that P(MVE-MA) is the most effective binder for Mn^{2+} with energy difference of only 6 kJ mol^{-1} to Fe^{3+} and Ca^{2+}

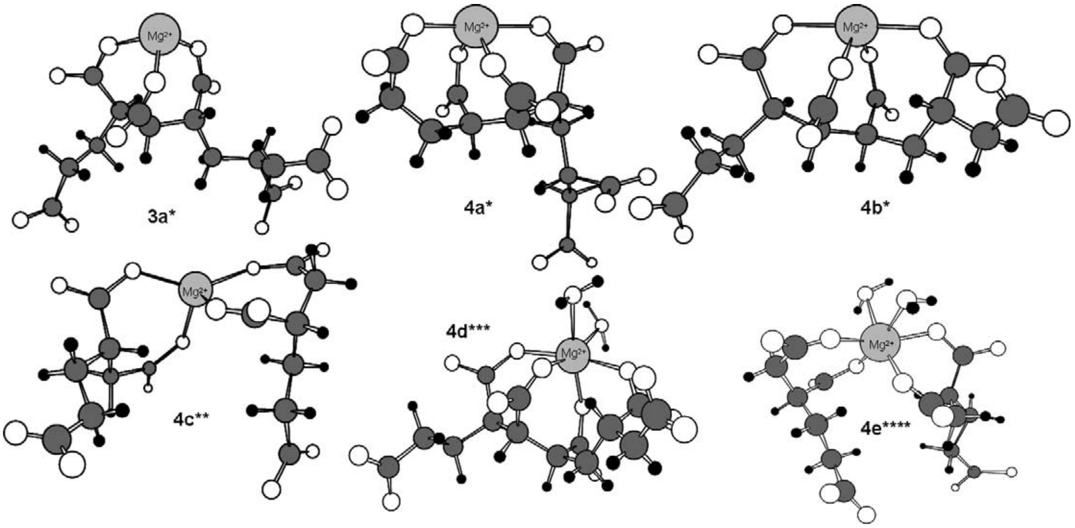

Fig. 3. Optimised Mg–P(AA-MA)-complexes. The geometries for all other metals are similar with only minor differences in bond lengths and angles. See Table 2 for energetics.

Table 3
3- and 4-Coordinated metal complexes of P(MVE-MA) dimer, their uncorrected and corrected complexation energies (in kJ mol^{-1})

Metal	Coord.	O_{ether}	O_{carbox}	ΔE_{co} (kJ mol^{-1})	ΔG_{c} (kJ mol^{-1})
Mg^{2+}	3a	0	3	−49	42
Ca^{2+}	3a	0	3	−47	30
Mn^{2+}	3a	0	3	−84	31
Fe^{3+}	3a	0	3	−252	32
Mg^{2+}	3b	1	2	−32	59
Ca^{2+}	3b	1	2	−30	47
Mn^{2+}	3b	1	2	−63	52
Fe^{3+}	3b	1	2	−204	80
Mg^{2+}	4a	1	3	−52	39
Ca^{2+}	4a	1	3	−49	28
Mn^{2+}	4a	1	3	−93	22
Fe^{3+}	4a	1	3	−256	28
Mg^{2+}	4b	1	3	−12	79
Ca^{2+}	4b	1	3	−12	65
Mn^{2+}	4b	1	3	−52	63
Fe^{3+}	4b	1	3	−207	77
Mg^{2+}	4c	2	2	22	113
Ca^{2+}	4c	2	2	10	87
Mn^{2+}	4c	2	2	−24	91
Fe^{3+}	4c	2	2	−135	149
Mg^{2+}	4d[a]	1	3	−68	23
Ca^{2+}	4d[a]	1	3	−52	25
Mn^{2+}	4d[a]	1	3	−90	25
Fe^{3+}	4d[a]	1	3	−266	18

O_{ether} refer to the number of metal-coordinating hydroxyl oxygen atoms and O_{carbox} to the number of metal-coordinating carboxylate oxygen atoms, respectively. See Fig. 4 for geometries.

[a] One ligand with two explicit water molecules.

and 11 kJ mol^{-1} to Mg^{2+}. In general, the complexation energies are at the same level as in the case of P(AA-MA) dimer ligand (Table 2) with the exception of Fe^{3+} ion, whose complexation energy with P(MVE-MA) is noticeably (24 kJ mol^{-1}) higher than with P(AA-MA). This clearly indicates that trivalent iron favours to complexate with four carboxylate oxygens instead of three carboxylate oxygens and one ether oxygen while the divalent metal ions prefer complexation only with three carboxylate oxygens.

In order to 'fill' the undercoordinated first solvation shell of metal ions, we optimised structure **4a** with two explicit water molecules. As seen in Fig. 4 and Table 3, complexation geometries do not change a lot. The complexation energies, on the other hand, were found to decrease for all the metal ions. The orientation of water molecules is slightly disturbed but no clear hydrogen bonds between water molecules and carboxylate oxygens of the ligand are formed.

3.2.3. Metal complexes of PESA

One point to notice for the PESA oligomer is its length and its effect to its complexation behaviour with different metal ions. Alkaline earth metals, especially Ca^{2+}, have been found to favour complexation with hydroxyl oxygen atoms while the transition metals coordinate to negatively charged carboxylate groups. [12] For this reason, one would expect that calcium prefers shorter oligomers or simply coordination to the end of the oligomer (where the hydroxyl oxygens are, respectively) and for transition metals, the coordination sites are more in the middle of the oligomer ligand. However, for computational reasons, in this study we have chosen n (Fig. 1) to be one. The most favourable structures, their coordination modes and complexation energies are shown in Table 4. Fig. 5 shows the corresponding structures for Mg^{2+}.

As seen in Table 4, all the metal ions except calcium favour coordination number of five with PESA. For Ca^{2+}, the 6-coordinated structure is more favourable with an energy difference of 7 kJ mol^{-1}. Comparison of the corrected complexation energies indicate that the PESA oligomer is the most effective binder for Ca^{2+} and Mn^{2+} ions and less effective for Fe^{3+} and Mg^{2+}. However, for all metal ions, complexation energies are lower (more negative) than for the previously studied metal complexes of poly(acrylic acid) and poly(α-hydroxy acrylic acid) oligomers [7].

For Mg^{2+}, Mn^{2+}, and Fe^{3+} the most favourable complexation geometry was found to be a 5-coordinated structure (Fig. 5) with four metal-coordinating carboxylate oxygen atoms and one ether oxygen atom. Ca^{2+}, on the other hand, favours a 6-coordinated structure with three metal-coordinating carboxylate oxygens, two ether oxygens and one hydroxyl oxygen. The importance of hydroxyl groups in Ca^{2+} ion binding was shown in our previous study with poly(α-hydroxy acrylic acid) ligand [7] and also in several experimental studies [12].

The electronic charge distribution is usually a useful tool for evaluating and comparing the complex structures in detail. In order to improve the understanding of ligands' behaviour with different metals we calculated the effective atomic charges for two complexes. Details are represented in Appendix A and the values are shown in Tables 5 and 6. The complexes include P(AA-MA) complex **4b*** and PESA complex **5d**. Unfortunately, in our cases there is two opposite charges very near each other and this will make the charge evaluation quite difficult. We do not consider the charges very reliable and they can be used only for quantitative analysis. It is clear that the ligands will strongly screen the metals charge since the computed charges do not agree well with the formal charge. We can conclude that the charge of ether oxygen is smaller than the carboxylate oxygen which would suggest that the ether oxygen binding would be weaker than the carboxyletes. Taking into account the large variations in the charge values the carboxylate oxygens will have similar charges in both complexes.

3.2.4. Comparison

Fig. 6 shows the complexation energies (in kJ mol^{-1}) for each metal with different ligands. Figure include also the oligomer ligands that were studied previously (poly(acrylic acid) (PAA) and poly(α-hydroxy acrylic acid) (PHA), respectively) [7].

Fig. 6 shows that when all the studied oligomeric ligands are taken into account, the most effective binder for all the metal ions is poly(epoxy succinic acid). The second most effective chelating agent for all the divalent metal ions was found to be poly(α-hydroxy acrylic acid). Trivalent iron clearly favours

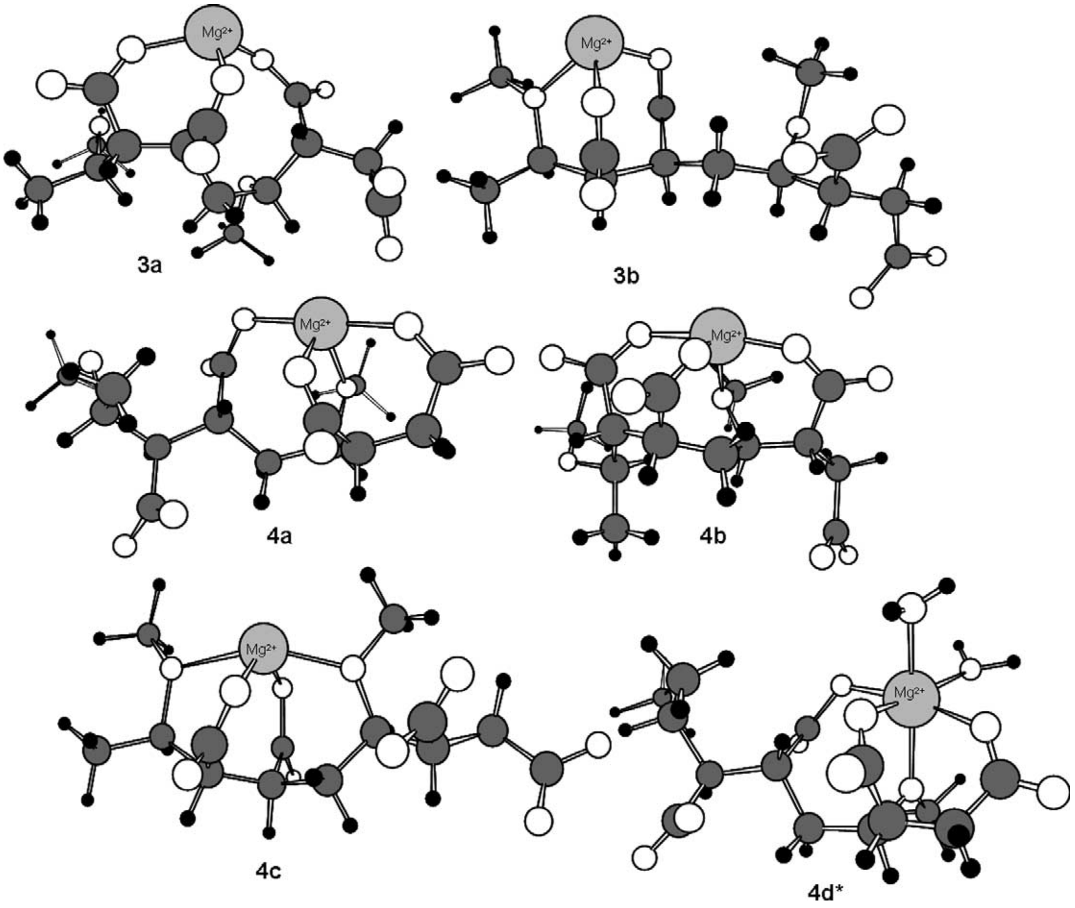

Fig. 4. Optimised Mg–P(MVE-MA)-complexes. The geometries for all other metals are similar with only minor differences in bond lengths and angles. The structure **4d*** is the structure **4a** reoptimised with two explicit water molecules. See Table 3 for energetics.

poly(acrylic acid) (modelled with dimer and trimer oligomers, respectively) over poly(α-hydroxy acrylic acid) and also for manganese the difference between the binding ability of PAA and PHA was found to be very slight.

Table 7 shows the metal specific coordination trends with different ligands in more detail. This data shows that there is no clear correlation between the metal–ligand coordination number and the complexation energy. In other words, the complexes with high coordination numbers are not by the default more favourable than the complexes with lower coordination numbers. The more important thing that affects the complexation capacity seems to be the structure of the oligomer backbone, more specifically its flexibility. Poly(epoxy succinic acid) chain with ether oxygen atoms is much more flexible than backbones that consist only of carbon atoms and thus, higher coordination numbers and better binding capability are achieved.

The most common metal coordinating atoms are carboxylate oxygens which are favoured especially by transition metal ions. This difference between transition and alkaline earth metal ions is seen in particular in the dimer–trimer type complexes of PAA and P(AA-MA). The significance of hydroxyl oxygens in metal ion binding was found to be greater for alkaline earth metals, especially for Ca^{2+}.

Table 7 also illustrates the energetic of metal–oligomer-complexes. In general, the corrected complexation energies are just slightly, if at all, negative, and thus, the conclusion might be that the studied ligands do not perform very well as chelators. However, if we compare obtained energies to our first study [6], where the metal complexes of seven (amino) polycarboxylic acids were studied, we see that for Mg^{2+} and Ca^{2+} ions, only DTPA performs better than PESA oligomer (corrected complexation energies, ΔG_{C2}, for DTPA complexes of Mg^{2+} and Ca^{2+} are -68 and -82 kJ mol^{-1}, respectively).

Table 4
5- and 6-Coordinated metal complexes of PESA, their uncorrected and corrected complexation energies

Metal	Coord.	O_{hyd}	O_{ether}	O_{carb}	ΔE_{co} (kJ/mol)	ΔG_c (kJ/mol)
Mg^{2+}	5	–	2	3	−134	−43
Ca^{2+}	5	–	2	3	−138	−61
Mn^{2+}	5	–	2	3	−171	−56
Fe^{3+}	5	–	2	3	−331	−47
Mg^{2+}	6	1	2	3	−106	−15
Ca^{2+}	6	1	2	3	−145	−68
Mn^{2+}	6	1	2	3	−151	−36
Fe^{3+}	6	1	2	3	−300	−16

See Fig. 5 for geometries.

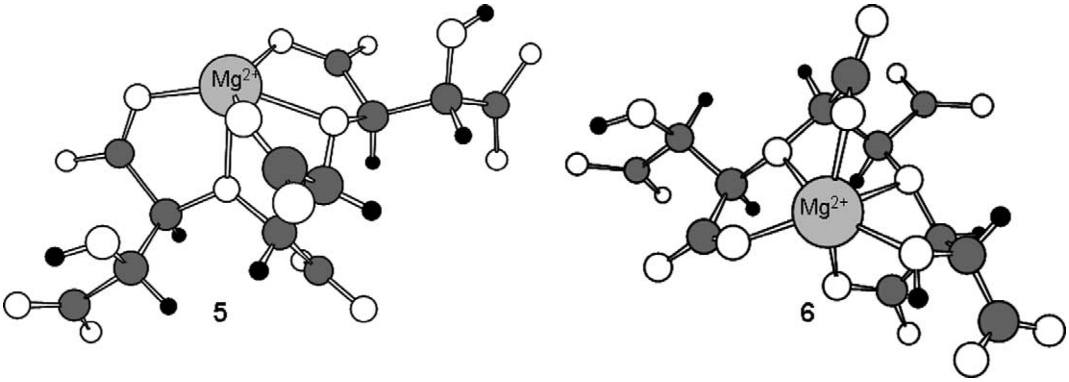

Fig. 5. Two optimised Mg–PESA-complexes. The geometries for all other metals are similar with only minor differences in bond lengths and angles. See Table 4 for energetics.

For transition metal ions, on the other hand, especially for Fe^{3+}, the studied oligomers seem to be poorer chelators than the studied (amino) polycarboxylic acid ligands with respect to the obtained complexation energies. Fig. 7 shows the (uncorrected) complexation energies for Mn^{2+} and Fe^{3+} complexes of PESA in comparison to the previously studied (amino) polycarboxylic acid ligands.

Fig. 7 shows that for Mn^{2+} PESA performs better than most of the studied (amino) polycarboxylic acids (only the complexes of DTPA, EDTA, and AES have lower ΔE_{CO} values, respectively) while for Fe^{3+}, all the nitrogen containing complexation agents perform clearly better than PESA. Only the nitrogen-free ODS shows comparable complexation behaviour for Fe^{3+}. This leads us to a conclusion that trivalent iron favours nitrogen atoms in complexation.

4. Discussion

Obtained minimum energy geometries indicate that the metals are not completely shielded (with the exception of 6-coordinated $[CaPESA]^{4-}$ complex) by the oligomer ligand. However, the addition of explicit water molecules does not change the local metal–ligand bonding pattern, and thus, the continuum solvent description performs well. The lack of experimental (thermodynamical) data makes the direct evaluation of the complexation properties of these ligands problematic, but, as demonstrated in our previous study with poly(acrylic acid) and poly(α-hydroxy acrylic acid), the experimental binding degrees can be produced by the method applied here.

Table 5
The atomic charges (in *e*) in P(AA-MA) complex **4b***

	Metal	O_{carb}	O_{carb}	O_{carb}	O_{carb}	Average O_{carb}
Mg^{2+}	1.41	−0.91	−0.86	−0.89	−0.96	−0.91
Ca^{2+}	0.07	−0.63	−0.45	−0.29	−0.67	−0.51
Mn^{2+}	−0.04	−0.61	−0.38	−0.28	−0.63	−0.48
Fe^{3+}	1.36	−0.71	−0.60	−0.53	−0.69	−0.63
Free ligand	–	–	–	–	–	−0.80

For free ligand, the average values of metal-coordinating oxygens is shown.

Table 6
The atomic charges (in *e*) in PESA complex **5d**

	Metal	Average O_{carb}	Average O_{ether}
Mg^{2+}	1.26	−0.83	−0.45
Ca^{2+}	0.67	−0.69	−0.27
Mn^{2+}	0.44	−0.61	−0.23
Fe^{3+}	0.84	−0.61	−0.28
Free ligand	–	−0.75	−0.47

For oxygen the average is over the metal-coordinating oxygens.

One interesting point to notice is that the ligands were not found to be very metal specific. Poly(epoxy succinic acid) oligomer is clearly the best chelator for all the studied metal ions and, if considered only the complexes with one ligand, poly(acrylic acid) is the least effective. That means that by modelling only one metal with different ligands the complexation behaviour of ligands can be evaluated in an approximate way. This conclusion can be made also on the basis of our first study [6] where the complexation behaviour of seven (amino) polycarboxylic acids with different metals was studied. The best chelators for all the metal ions were found to be DTPA and EDTA (in this order), which is also consistent with experimental data. However, as seen in the case of DTPA, differences in complexation modes may occur between the metals and for this reason, the optimisations and the energy calculations should be repeated for all the metals separately.

5. Conclusions

In this study, we have employed a method based on BP86-continuum solvation geometry optimisations with (previously determined) empirical corrections to the final energy to study the complexation properties of polycarboxylic acid ligands, poly(acrylic acid-*co*-maleic acid) (P(AA-MA)), poly(methyl vinyl ether-*co*-maleic acid) (P(MVE-MA)), and poly(epoxy succinic acid) (PESA). In addition to free oligomers their complexes with Mg^{2+}, Ca^{2+}, Mn^{2+}, and Fe^{3+} with P(AA-MA), P(MVE-MA), and PESA oligomers are reported.

When all the studied oligomer ligands are taken into account, the most effective ligand for all the metal ions was found to be poly(epoxy succininc acid). With PESA, Ca^{2+}

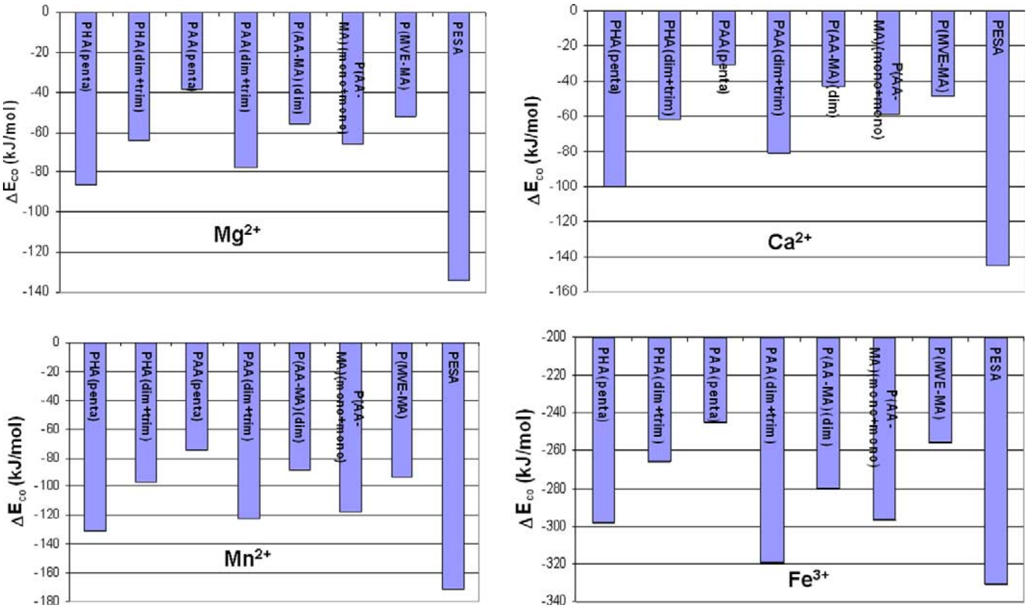

Fig. 6. The (uncorrected) complexation energies for metal ions with different ligands.

Table 7
Coordination trends of different ligands and corrected complexation energies

Ligand\metal	ΔG_c (kJ/mol) Mg^{2+}	ΔG_c (kJ/mol) Ca^{2+}	ΔG_c (kJ/mol) Mn^{2+}	ΔG_c (kJ/mol) Fe^{3+}	Charge[a]	Coord.	O_{hyd}	O_{carbox}	O_{ether}
PHA (penta)	5[b]	−23	−16	−14	−3	4 (5 for Mg^{2+})	2 (3 for Mg^{2+})	2 (1 for Mg^{2+})	–
PHA (dim+trim)	27	15	18	19	−3	6	3	3	–
PAA (penta)	52	46	40	39	−3	3	–	3	–
PAA (dim+trim)	14	−4	−7	−35	−3	5 (4 for Mn^{2+})	–	5 (4 for Mn^{2+})	–
P(AA-MA) (dim)	36	34	27	4	−4	3 (4 for Fe^{3+})	–	3 (4 for Fe^{3+})	–
P(AA-MA) (mono+mono)	25	18	−2	−13	−4	4	–	4	–
P(MVE-MA)	39	28	22	28	−2	4	–	3	1
PESA	−43	−68	−56	−47	−4	5 (6 for Ca^{2+})	0 (1 Ca^{2+})	3	2

[a] The charge refers to total charge of M^{2+}–L-complexes. Therefore, for trivalent iron, the total charge of complex is charge shown in Table 1.

[b] For Mg^{2+} the 4-coordinated structure is energetically only 2 kJ mol^{-1} higher the most favourable 5-coordinated complex. Thus, both of these complexes are very likely present.

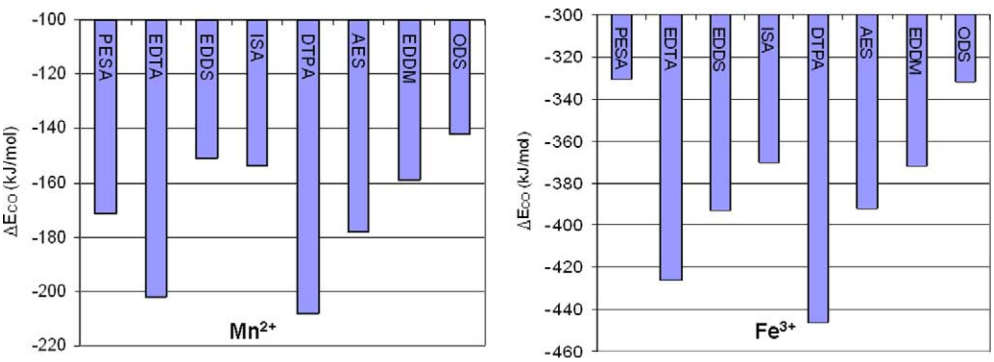

Fig. 7. The (uncorrected) complexation energies for Mn^{2+} and Fe^{3+} with PESA and previously studied (amino) polycarboxylic acids (all the values except those of PESA complexes are taken from Ref. [6]).

favoured coordination number of six with one metal-coodinating hydroxyl oxygen atom while the other metals (Mg^{2+}, Mn^{2+}, and Fe^{3+}) were found to favour 5-coordinated complexation geometry (with 3 metal-coordinating carboxylate oxygens and 2 ether oxygens, respectively). Energetically, PESA oligomer was found to be very efficient chelator for Mg^{2+} and Ca^{2+}, also when the previously studied (amino) polycarboxylic acid ligands are taken into account.

The minimum energy geometries are reasonable and they indicate that metals are not completely shielded by oligomer ligands. The addition of explicit water molecules in the first coordination shell of metal ions does not change considerably the complexation geometry.

In this study as well as in our previous study [7], our aim was to test the previously developed method [6] for oligomeric ligands and their local complexation properties. It is obvious that further studies are needed and therefore, all the studied ligands and their complexation properties will be further studied by the means of molecular dynamics. This opens the possibility to take into account the effect of counter ions and macroscopic properties of polymers.

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Appendix A. The electrostatic charge distribution

We have calculated the effective atomic charges for the metal complexes of P(AA-MA) (structure **4b***) and PESA (structure **5d**) using the density functional theory and the electrostatic potential (ESP) method (the Merz–Kollman scheme). For the reference, we have calculated the charges also for the free oligomers. The COSMO-optimised structures were used for the calculations. All the calculations have been performed with Gaussian 03 [15], using the BLYP density functional [16] and 6-31G(d,p) basis set. For Mn^{2+} and Fe^{3+}, we used the radii of 2.0 Å in the ESP-calculations, and for Ca^{2+}2.3 Å. We performed also some calculations using the Hartree–Fock theory but the charges were observed to differ quite a lot from DFT results and therefore, we postpone the quantitative (and more detailed) analysis of charge distribution in metal complexes with different metal-coordinating groups (including amino groups of previously studied ligands) in future and represent the obtained results here in a qualitative way.

The calculated charges (in units of *e*) are shown in Tables 5 and 6. Only the charges for the metal ions and metal-coordinating atoms are shown. As the charges in free oligomers were observed to be quite similar for different oxygen atoms, only the average values are shown in Tables.

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