Available online at www.sciencedirect.com
SCIENCE DIRECT®

ELSEVIER

Polymer 46 (2005) 12641–12652

polymer

www.elsevier.com/locate/polymer

Density functional complexation study of metal ions with poly(carboxylic acid) ligands. Part 1. Poly(acrylic acid) and poly(α-hydroxy acrylic acid)

Henna Pesonen [a,c,1], Atte Sillanpää [a,1], Reijo Aksela [b,2], Kari Laasonen [c,*]

[a] Department of Chemistry, University of Naples 'Federico II', I-80126 Naples, Italy
[b] Kemira Oyj, Espoo Research Center, P.O. Box 44, FIN-02271, Espoo, Finland
[c] Department of Chemistry, University of Oulu, P.O. Box 3000, FIN-90014 Finland

Received 2 September 2005; received in revised form 12 October 2005; accepted 12 October 2005
Available online 2 November 2005

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) (PAA) and poly(α-hydroxy acrylic acid) (PHA) oligomers. The complexation energies for Mg^{2+}, Ca^{2+}, Mn^{2+}, Fe^{3+}, and Zn^{2+} with one oligomer ligand (pentamer), and two ligands (dimer and trimer) have been calculated. The nature of hydrogen bonding in PHA has been studied both in free oligomers and in metal complexes. The obtained binding degrees are in good agreement with experimental results although with quite small energy differences. The complexation energies were found to be very sensitive to changes in internal hydrogen bonds. The role of hydroxyl oxygen atoms in metal ion binding was observed to be more important for Ca^{2+} than for other metals.

Keywords: Metal ion complexation; Ab initio calculations; Binding energies

1. Introduction

Complexation is a very efficient way to inactivate and remove metal ions. Many heavy metals, e.g. lead and chromium are directly toxic to humans [1], but they can also be a problem in different industrial processes.

From the viewpoint of the paper industry, the most problematic metal ions are manganese and iron, which catalytically decompose hydrogen peroxide and peracids which are used in the pulp bleaching processes [2]. Pulp contains not only these harmful metal ions but also magnesium and calcium. Mg^{2+} has actually been found to be beneficial to the bleaching process, and Ca^{2+} is inactive and its complexation only consumes the complexating agent. The widely used and efficient complexing agents, such as EDTA (ethylene diamine tetraacetic acid) and DTPA (diethylenetriamine pentaacetic acid), display low biodegradability [3]. Furthermore, they are able to mobilise heavy metals from sediments in natural waters. Thus, it is important to develop and study more environmentally friendly complexing agents. One interesting group of these includes (nitrogen free) poly(carboxylic acids), e.g. poly(acrylic acid) and poly(α-hydroxy acrylic acid).

The most common poly(carboxylic acids), e.g. poly(acrylic acid), are weak acids and their pK_a values are linearly dependent on the degree of proton dissociation, α [4]. This has been explained by the electrostatic interaction between negatively charged carboxylate groups in the polymer [5]. For the polymers with higher charge density, e.g. poly(maleic acid), on the other hand, a sharp increase in pK_a has been reported at ca. $\alpha = 0.5$. This interesting property has been thought to be related to intramolecular hydrogen bonding between the dissociated and undissociated carboxyl acid groups [6]. According to these previous experimental studies, internal hydrogen bonds have been shown to have a very clear effect on properties and behaviour of polyelectrolytes.

The dissociation behaviour of weak polyacids has been studied widely by experimental methods [4,7]. Metal ion binding properties of poly(acrylic acid) (PAA) have been studied by equilibrium dialysis [8], thermogravimetry, and spectroscopic methods [9]. PAA has been found to be the most

---

* Corresponding author. Tel.: +358 8 533 1640; fax: +358 8553 1603.
E-mail addresses: henna.pesonen@oulu.fi (H. Pesonen), atte.sillanpaa@csc.fi (A. Sillanpää), reijo.aksela@kemira.com (R. Aksela), kari.laasonen@oulu.fi (K. Laasonen).
[1] Tel: +39 081 674 212; fax: +39 081 674 090.
[2] Tel: +358 1061 516; fax: +358 10862 2000.

0032-3861/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2005.10.069

effective binder for Cu^{2+}, Ca^{2+} and Ni^{2+} but less effective for Mg^{2+} [8,9].

Poly(α-hydroxy acrylic acid) (PHA) is an interesting poly(carboxylic acid) with a strong tendency to form internal hydrogen bonds and lactone rings under different pH conditions. Its lactone ring formation, dissociation and swelling behaviour have been studied by means of NMR, UV, and IR spectroscopies, and potentiometric titrations [4,10–13]. It has been shown [13] that the lactone ring is more stable than a COOH group when the degree of dissociation, α is greater than 0.5. Actually, COOH-groups are present only when $\alpha < 0.5$ (pH < 4). Experimentally PHA has been shown to be the most effective binder for Zn^{2+} and Ca^{2+}, but less effective for Mg^{2+} [8].

Most of the earlier studies related to metal ion binding properties of PAA and PHA are experimental and thus, we find it both relevant and interesting to study this issue also by computational methods. The well-known complexing agents for cations, e.g. crown ethers, have been widely studied both by experimental [14] and computational [15] methods, but little attention has been paid to the computational studying of polyelectrolytes and their complexation properties. Some earlier studies [12,13] related to dissociation and swelling behaviour of PHA include computational results for free a PHA dimer and tetramer calculated at HF/3-21G level in the gas phase. However, to our knowledge this is the first complexation study of PAA and PHA based on density functional methods (DFT) with a continuum solvation model.

In a previous study [16], we investigated complexation of metal ions with (amino)polycarboxylic acid ligands using DFT-COSMO and Car-Parrinello ab initio molecular dynamics. As a result, a fast and straightforward computational method for evaluating the performance of complexing agents was developed. The aim of this present study was to test the computational method for polymeric ligands and their metal complexes. Unlike in the previous study, here geometries were optimised with the COSMO-solvation model. Complexation energies for Mg^{2+}, Ca^{2+}, Mn^{2+}, and Fe^{3+} with PAA and PHA oligomers were determined and they were corrected using the previously determined empirical correction parameters. For the Zn^{2+} ion, we have optimised only those geometries that were observed to be the most favourable for other metal ions. The purpose was to compare the obtained binding degrees with experimental results and thus to evaluate the general performance of the method. In addition to complexation geometries, we have investigated also the nature of internal hydrogen bonding in free PHA oligomers.

2. Computational details

All DFT-calculations have been performed using the program TURBOMOLE [17]. We have employed the TZVP basis set for all atoms and the BP86-functional [18] throughout the study. The RI-approximation [19] has been used to speed up the calculations. All geometries have been optimized using the COSMO-solvation model [20]. The determination of the COSMO-radii for metal ions is described in Section 3.3, otherwise the default options in the program TURBOMOLE have been used. For the transition metal complexes (except those of Zn^{2+}) we have employed the spin unrestricted formalism and for the earth alkaline metal complexes (and those of Zn^{2+}) 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, concentrating on the properties of poly(α-hydroxy acrylic acid). Then, we will present the results for metal complexes of poly(α-hydroxy acrylic acid) and poly(acrylic acid), and in the end of this section, we will make some comparisons pertaining to the complexation properties of these two ligands. General considerations on the applicability of this method are discussed in Section 4. Monomer units of poly(α-hydroxy acrylic acid) and poly(acrylic acid) are shown in Fig. 1.

3.1. Poly(α-hydroxy acrylic acid) oligomers

In order to study the nature of internal hydrogen bonding of poly(α-hydroxy acrylic acid) (PHA), we optimised the dimer, trimer, and pentamer structures. Isotactic, syndiotactic, and atactic configurations of each oligomer were considered. Oligomers were terminated with hydrogen atoms. Molecular mechanics (MM2) was used to create the starting configurations for oligomers.

The bleaching process is carried out at very high pH value (10–11). At this pH, most of the carboxylic acid groups are dissociated. According to experimental studies of Tamura et al. [13], the degree of dissociation α for PHA at pH 9.6 is 0.971. Thus, we assumed all carboxylic acid groups to be deprotonated in our optimisations.

Ten pentamer, three dimer, and three trimer structures are shown in Table 1, including the definition of the oligomers' stereochemistry and the number of hydrogen bonds formed within one monomer unit. The total numbers of optimised oligomers are 15 for pentamer, and 5 for both trimer and dimer, respectively. As we found many of these geometries very similar to each other both energetically and structurally (internal hydrogen bonds), we did not find it relevant to include all of them in Table 1. The energetically most

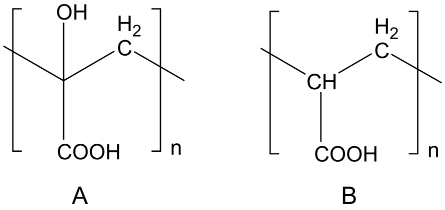

Fig. 1. Monomer units of poly(α-hydroxy acrylic acid) (A) and poly(acrylic acid) (B).

Table 1
Description of the structures for PHA pentamers, dimers and trimers, stereochemistry, and the sum of hydrogen bonds formed within each monomer unit

Geometry	ΔE (kJ mol^{-1})	Stereochemistry[a]	Intramonomer hydrogen bonds
Penta 1	21	rrrrs	1
Penta 2	23	rrrrs	5
Penta 3	7	rrrrs	2
Penta 4	11	rrrrs	3
Penta 5	9	rrrrs	2
Penta 6	31	rrrrs	4
Penta 7	11	rrrrs	1
Penta 8	9	rrsrs	2
Penta 9	11	srsrs	3
Penta 10	0	rrsrs	1
Dimer 1	28	ss	1
Dimer 2	18	sr	0
Dimer 3	0	rs	2
Trimer 1	8	rrr	2
Trimer 2	7	rrr	2
Trimer 3	0	rsr	3

ΔE is the deviation (in kJ mol^{-1}) from the lowest energy stucture (penta 10, dimer 3 and trimer 3, respectively).

[a] See Appendix for the details of the description of stereochemisty.

favourable oligomer structures are shown in Fig. 2 together with their COSMO-corrected total energies (in a.u.). Hydrogen bonds are represented with dotted lines, their lengths (O···H, in Ångströms) and angles (O···H–O, in degrees) are shown also in Fig. 2.

As shown in Fig. 2, the PHA pentamer can form internal hydrogen bonds between the donor (OH) and any of the acceptors (OH, COO^{-}) both within the same monomer unit and to other monomer units. The oxygen atom of an OH group can also act as a hydrogen bond acceptor and there is one hydrogen bond of this type in the lowest energy pentamer structure shown in Fig. 2. The O···H hydrogen bond distances in all pentamer structures vary between 1.669 and 1.903 Å, and O···H–O angles between 124 and 174 degrees.

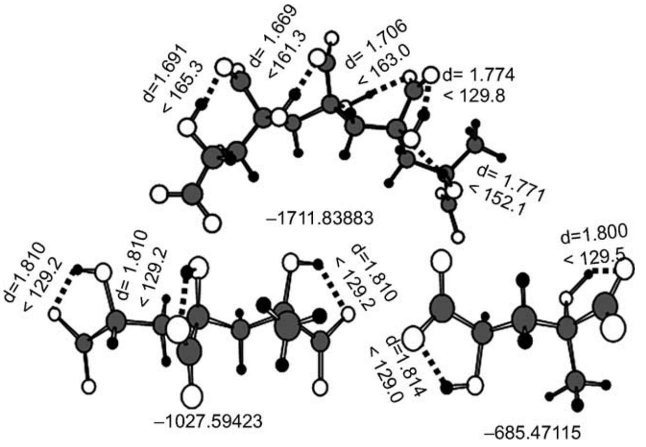

Fig. 2. Optimised structures for PHA pentamer, trimer, and dimer. Hydrogen bonds are represented with dotted lines, their lengths (H···O, *d*, in Ångströms) and angles (O···H–O, <, in degrees) are shown. Total energies (in a.u.) are shown below the structure. White spheres depict oxygen atoms, black spheres hydrogen, and dark gray carbon atoms.

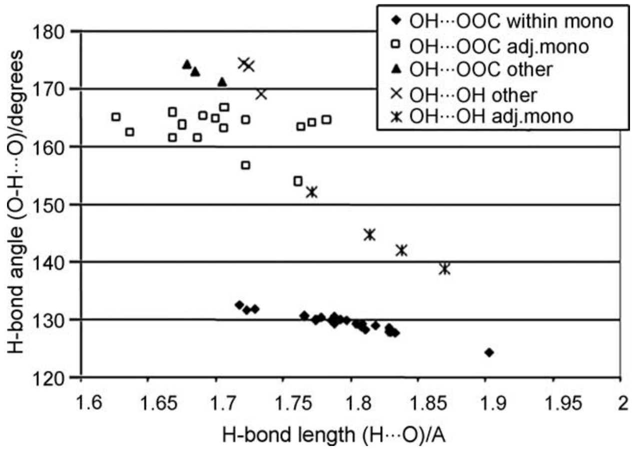

Fig. 3. Hydrogen bond angle (O···H–O/degrees) in PHA pentamer structures as a function of hydrogen bond length (H–O/Ångströms).

Internal hydrogen bonds of the PHA pentamers can be divided in five categories on the grounds of the hydrogen bond acceptor atom and its location. Fig. 3 shows the relationship between the hydrogen bond angle and length of these different types of hydrogen bonds in PHA pentamers. The total number of pentamer structures included in figure is 10, and because every OH group was found to act as a hydrogen bond donor, the total number of data points in Fig. 3 is 50.

Fig. 3 shows that the most linear hydrogen bonds occur between monomers which are separated by one or more monomer units (‘OH···OOC other’ and ‘OH···OH other’, respectively). The hydrogen bonds that are formed within one monomer unit are longer and, more clearly, less linear, and, therefore, energetically less favourable. Even so, in the lowest energy pentamer structure, there is one hydrogen bond of this type. Bond lengths and angles of these intramonomer hydrogen bonds are in good agreement with the gas phase result for a PHA dimer obtained by Tamura et al. at HF/3-21G level (126.9° and 1.816 Å) [13]. In general, these internal hydrogen bonds can be considered strong hydrogen bonds. In liquid water, the hydrogen bond length (O···H) is about 1.8 Å and most of the observed hydrogen bonds in PHA pentamers are shorter than that. However, it is known that BP86 functional, as well as BLYP, B3LYP and B3B86, underestimate the strong hydrogen bond-type interactions compared to experimental values [21]. On the other hand, as the interactions between a solvated molecule and the solvent are not described explicitly, the formation of internal hydrogen bonds can be considered to be more favourable in our model based on BP86/COSMO-approach than in the ‘real’ solution.

Compared to the optimized dimer and trimer structures, the variation in internal hydrogen bonding in pentamers was found to be broader. In the most favourable PHA dimer and trimer structures, all hydrogen bonds were formed within the same monomer unit. This indicates that the dimer and trimer structures cannot be used if one wants to study the nature of hydrogen bonding of the entire polymer PHA (at this level of theory). In the case of PHA, a pentamer turned out to be a ligand of reasonable size for DFT/COSMO optimisations. The

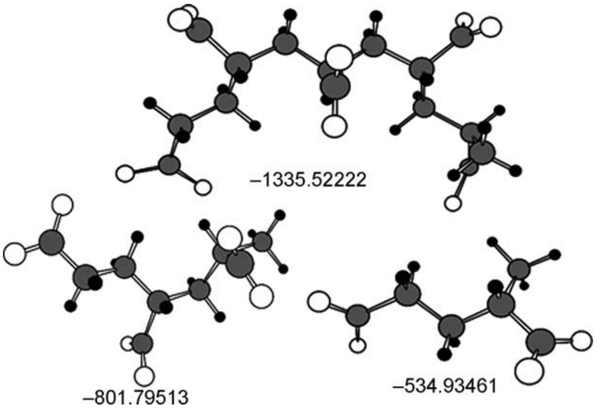

Fig. 4. Optimised structures for PAA pentamer, trimer, and dimer. Total energies (in a.u.) are shown below the structure. See caption of Fig. 2 for atom colours.

macroscopic properties of a polymer, e.g. folding, obviously can not be studied with this approach, but as will be shown below, five monomer units is enough to describe local metal coordination.

PHA is able to form lactone rings between neighbouring COOH and OH groups. Lactone ring formation is strongly dependent on the system pH, so that under slightly alkaline conditions (pH 8.23) almost one fourth of the carboxylate groups (23.7 mol%) are in lactone rings [13]. The peroxide bleaching process takes place at the pH value of 10–11. At this pH value almost all carboxylic acid groups are deprotonated, and no lactone rings are present. Even though the understanding of the mechanism and energetics concerning lactone ring formation at different pH conditions would be an interesting and demanding issue to study it will be postponed to a future publication. In this contribution, we justifiably (see above) assumed all COO^- groups to be deprotonated.

3.2. Poly(acrylic acid) oligomers

The uncomplexed polyacrylic acid was studied as already described for PHA by optimising several structures for dimers, trimers, and pentamers. As in the case of PHA, total deprotonation of carboxylic acid groups was assumed and oligomers were terminated with hydrogen atoms. The energetically most stable PAA oligomer structures are shown in Fig. 4, together with their COSMO-corrected total energies (in a.u.). There are no hydrogen bond donor groups in deprotonated PAA oligomers, so the role of the internal hydrogen bonds is not an issue in this case. As shown in Fig. 4, the minimum energy structures have the negatively charged carboxylate groups as far away from each other as possible due to the repulsive Coulomb interaction between them.

3.3. Metal ion solvation energies/hexa aquo complexes

The optimisation of the metal complexes using the continuum solvation model without explicit water molecules requires effective radii for the metal atoms. Previously, we have used gas phase optimised geometries and a single point continuum solvation calculation to obtain the total energy in solution [16]. In the present study, we have used exclusively COSMO-optimised structures and, therefore, we recalculated the effective metal radii according to Eq. (1):

$$\Delta E_{\mathrm{solv}}(\mathrm{M}^{m+}) = \Delta E_{\mathrm{CO}}(\mathrm{M}^{m+})$$

$$= E_{\mathrm{CSM}}\left(\mathrm{M(H_2O)}_6^{m+}\right) - E_{\mathrm{vac}}(\mathrm{M}^{m+}) - 6E_{\mathrm{CSM}}(\mathrm{H_2O}) \qquad (1)$$

where $E_{\mathrm{CSM}}(\mathrm{X})$ is the COSMO-corrected total energy of species (X). Eq. (1) essentially states, that the metal is given a radius which gives the same solvation energy without explicit water molecules as the corresponding hexahydrate, which can be calculated without a predetermined metal radius (see Ref. [16] for more details and evaluation of this method). The determined COSMO radii for metal ions and their solvation energies are given in Table 2.

Table 2 shows that the COSMO radii obtained by COSMO-optimised hexahydrates are in practice identical to the earlier results obtained by corresponding gas phase optimisations [16]. The metal ion solvation energies are within 10 kJ mol^{-1} from the gas phase geometry results but still differ quite a lot from experimental results, especially in the case of the Fe^{3+} ion.

3.4. Metal complexes

We have performed geometry optimisations for metal complexes of PHA and PAA pentamers to obtain the minimum energy complex structures. Roughly 30 (20 for PHA and 10 for PAA, respectively) different coordination modes and geometries were studied. Also, different stereochemical configurations for the ligands have been taken into account. All different bonding configurations were separately optimised for

Table 2
COSMO-radii (in Ångströms) and solvation energies (in kJ mol^{-1}) for metal ions

Metal ion	r_{CSM} [a]	ΔE_{CO} [a]	r_{CSM} [b]	ΔE_{CO} [b]	ΔG_{exp} [c]	r_{av} [d]
Mg^{2+}	1.456	−1909	1.452	−1907	−1906	2.095
Ca^{2+}	1.825	−1523	1.824	−1522	−1593	2.435
Mn^{2+}	1.467	−1906	1.472	−1903	−1832	2.180
Fe^{3+}	1.391	−4503	1.393	−4494	−4333	2.022
Zn^{2+}	1.342	−2082	1.344	−2081	−2028	2.098

[a] Values obtained by using Eq. (1).
[b] Values taken from Ref. [16].
[c] Experimental free energy of solvation from Ref. [22].
[d] Average metal–oxygen distance in optimised hexahydrates (Å).

Table 3
Correction parameters for metal ions (in kJ mol^{-1}), see Ref. [16] for details

Metal ion	Mg^{2+}	Ca^{2+}	Mn^{2+}	Fe^{3+}	Zn^{2+}
$\tilde{G}_{ML_i}$	91	77	115	284	116

Mg^{2+}, Ca^{2+}, Mn^{2+} and Fe^{3+} metal ions. In addition, some structures were optimised also for Zn^{2+}. Complexation energies were determined according to Eq. (2):

$$\Delta E_{CO} = \Delta E_{CSM} = E_{CSM}(ML^{n-m}) + 6E_{CSM}(H_2O) - E_{CSM}(L^{m-}) - E_{CSM}\left(M(H_2O)_6^{n+}\right) \quad (2)$$

where $E_{CSM}(X)$ is the COSMO-corrected total energy of species (X). M and L refer to metal and ligand, respectively. Since there are no experimental solvation free energy data for the metal–oligomer complexes available, and since based on previous similar calculations we expect large deviations from experimental complexation energies, ΔE_{CO} were corrected with the metal specific correction parameters, $\tilde{G}_{ML_i}$, determined previously for the same method applied to (amino)-polycarboxylic acid ligands, including, e.g. ethylenediamine tetraacetic acid (EDTA) and diethylenetriamine pentaacetic acid (DTPA). 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. (3):

$$\Delta G_C(M_i, L_j) = \Delta E_{CO}(M_i, L_j) + \tilde{G}_{ML_i} \quad (3)$$

The correction parameters are shown in Table 3 (values taken from Ref. [16]). 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 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.

3.4.1. Metal complexes of PHA

3.4.1.1. Metal complexes of PHA pentamer. PHA can coordinate to a metal ion in various ways. The formation of chelate rings stabilises the complex due to the so-called chelate effect. 5- and 6-membered chelate rings have been found to be the most favourable ones. In the case of PHA, a 5-membered chelate ring is formed when oxygen atoms of OH and COO^- groups of the same monomer unit coordinate to the metal ion. With this well-known detail in mind, we optimised metal complexes of PHA pentamers with different coordination numbers and modes in order to find the most favourable structure for complexation.

The metal coordination numbers in PHA pentamer complexes vary between 3 and 5. Table 4 displays eight different 4- and 5-coordinated structures and their complexation energies. The geometries of Mg^{2+}-complexes are shown in Fig. 5.

All metal ions, except Mg^{2+}, favoured the coordination number of 4 with the PHA pentamer. As shown in Fig. 5, in the energetically most favourable structure (**4a**) two carboxylate and two hydroxyl oxygen atoms in adjacent monomer units coordinate to the metal ion. Thereby, two 5-membered chelate rings are formed. For Mg^{2+}, a 5-coordinated structure (**5b**) with four metal-coordinating oxygen atoms from alcohol groups was 2 kJ mol^{-1} more favourable than the 4-coordinated structure **4a**. For Ca^{2+}, the same structure is only 7 kJ mol^{-1} higher than the 4-coordinated one. For transition metals (Mn^{2+} and Fe^{3+}), the 5-coordinated structure **5b** is noticeably (18 and 15 kJ mol^{-1}, respectively) less favourable than for alkaline earth metals.

Table 4 and Fig. 5 show that the most favourable stereochemical configuration of the ligand's binding site is syndiotactic. All three 4-coordinated geometries (**4a**, **4b**, and **4c**) with syndiotactic configuration in metal coordinating monomers are considerably more favourable than structure **4d** with an isotactic binding site. Even the 4-coordinated structure **4e** with three metal-coordinating hydroxyl oxygen atoms was found to be more favourable for all metal ions, except for Mn^{2+}, than structure **4d**.

By comparing the corrected complexation energies the efficiency of PHA in metal ion binding can be evaluated. The PHA pentamer is the most effective binder for Ca^{2+} and Zn^{2+} ions. For Mg^{2+}, PHA was found to be poor compared to other metals. Fe^{3+} and Mn^{2+} were observed to bind with similar strength with a difference of only 3 kJ mol^{-1}. Although the differences in corrected complexation energies are small, the obtained binding degree ($Ca^{2+} > Zn^{2+} > Mn^{2+} = Fe^{3+} > Mg^{2+}$) is in good agreement with the experimental results reported by Tamura et al. [8] in the cases of Ca^{2+}, Mn^{2+} and Mg^{2+} ions ($Ca^{2+} > Mn^{2+}$ and $Ca^{2+} > Mg^{2+}$). Experimental results for competitive binding of Zn^{2+} and Mn^{2+} ions ($Zn^{2+} > Mn^{2+}$) are also supported by our results with a quite tiny energy difference of 4 kJ mol^{-1}. For Fe^{3+}, there are no corresponding experimental data available. For Ca^{2+} and Zn^{2+}, the difference in corrected complexation energies is only 3 kJ mol^{-1}, therefore, they can be considered to bind almost in similar strength. In general, the differences in corrected complexation energies are very small and, therefore, one has to evaluate the obtained binding degree with certain criticism.

Another concern related to corrected complexation energies is that they are just slightly negative. This points to a conclusion that PHA is not a very efficient binder for metal ions. However, PHA is known for its ability to bind divalent metal ions and thus, the empirical correction parameters in this case are not very accurate. But as discussed at the end of Section 3.4 the trends should be correct but the absolute energies are not very accurate.

The third point connected to complexation energies is that they were discovered to be very sensitive to changes in internal hydrogen bonding. As shown in Table 4 and Fig. 5 (geometries

Table 4
4- and 5-coordinated metal complexes of PHA pentamers, their uncorrected and corrected complexation energies (in kJ mol^{-1})

Stereochemistry[a]	Metal	Coord.	O_{hyd}	ΔE_{csm} (kJ mol^{-1})	ΔG_{C2} (kJmol^{-1})
rRSrs	Mg^{2+}	4a	2	−85	6
rRSrs	Ca^{2+}	4a	2	−94	−17
rRSrs	Mn^{2+}	4a	2	−125	−10
rRSrs	Fe^{3+}	4a	2	−291	−7
rRSrs	Zn^{2+}	4a	2	−130	−14
rRSrs	Mg^{2+}	4b	2	−62	29
rRSrs	Ca^{2+}	4b	2	−70	7
rRSrs	Mn^{2+}	4b	2	−102	13
rRSrs	Fe^{3+}	4b	2	−249	35
sRSrs	Mg^{2+}	4c	2	−72	19
sRSrs	Ca^{2+}	4c	2	−73	4
sRSrs	Mn^{2+}	4c	2	−105	10
sRSrs	Fe^{3+}	4c	2	−219	65
rRRrs	Mg^{2+}	4d	2	−24	67
rRRrs	Ca^{2+}	4d	2	−38	39
rRRrs	Mn^{2+}	4d	2	−61	54
rRRrs	Fe^{3+}	4d	2	−186	98
rRSSr	Mg^{2+}	4e	3	−47	44
rRSSr	Ca^{2+}	4e	3	−50	27
rRSSr	Mn^{2+}	4e	3	−58	57
rRSSr	Fe^{3+}	4e	3	−253	31
rRRRs	Mg^{2+}	5a	3	−54	37
rRRRs	Ca^{2+}	5a	3	−80	−3
rRRRs	Mn^{2+}	5a	3	−98	17
rRRRs	Fe^{3+}	5a	3	−236	48
SSSRS	Mg^{2+}	5b	4	−87	4
SSSRS	Ca^{2+}	5b	4	−86	−9
SSSRS	Mn^{2+}	5b	4	−107	8
SSSRS	Fe^{3+}	5b	4	−273	11
RRSRS	Mg^{2+}	5c	5	−53	38
RRSRS	Ca^{2+}	5c	5	−79	−2
RRSRS	Mn^{2+}	5c	5	−72	43
RRSRS	Fe^{3+}	5c	5	−243	41

Stereochemisty and coordination mode of ligand are specified. O_{hyd} refer to the number of metal coordinating hydroxyl oxygen atoms.

[a] See Appendix for the details of the description of stereochemisty. Letters S and R refer to metal-bonding monomer units, s and r to ‘free’ monomer units, respectively.

4a and **4b**), a change in one hydrogen bond in a metal coordinating OH group caused an energy change of more than 20 kJ mol^{-1} for all metal ions.

The role of PHA hydroxyl oxygen atoms in different metal ion binding can be evaluated by comparing the complexation energies of 4- and 5-coordinated metal complexes with different numbers of metal-coordinating hydroxyl groups. As seen in Table 4 and Fig. 5, the coordination of the Ca^{2+} ion to hydroxyl oxygen atoms is notably more favourable than for other metal ions. In the case of Ca^{2+}, the OH and COO– are equally good binder, but for other metals the COO^- group form stonger bonds. For example, a 5-coordinated complex with five metal-coordinating hydroxyl oxygen atoms is energetically over 40 kJ mol^{-1} more favourable for Ca^{2+} than for other metal ions. This is a so called direct effect of α-OH groups on the binding ability of PHA, and has been investigated and discussed previously in experimental studies reported, e.g. by Tamura et al. [8] and Ogawara et al. [23] In the PHA complexes of Fe^{3+}, deprotonation of one metal coordinating OH group was found to occur. This has also been reported earlier in experimental studies, e.g. those of citrate–iron complexes [24].

The strength of hydrogen bonds in metal complexes can be analysed by comparing them to results obtained for free oligomers. In Fig. 6, the hydrogen bond lengths and angles formed between metal coordinating OH groups and COO^- groups of adjacent monomer units are shown. The figure includes data points from the energetically most favourable 4-coordinated complexes of Mg^{2+}, Ca^{2+}, Mn^{2+} and Zn^{2+}. The hydrogen bonds of Fe^{3+} complexes are excluded due to the deprotonation of metal coordinating OH groups.

The Fig. 6 shows that hydrogen bonds formed between a metal-coordinating OH group and a COO^- group from the neighbouring monomer unit are shorter and more linear than the corresponding hydrogen bonds in a free oligomer. These strong hydrogen bonds may be considered as a stabilising factor for metal complexes. In addition, they may also have an effect on the macroscopic properties of polymer, which cannot be studied by this method.

3.4.1.2. Metal complexes of PHA dimer and trimer. The highest obtained coordination number for the PHA pentamer ligand was five (see Table 4 and Fig. 5). In order to study the possibility of complexes with higher coordination numbers

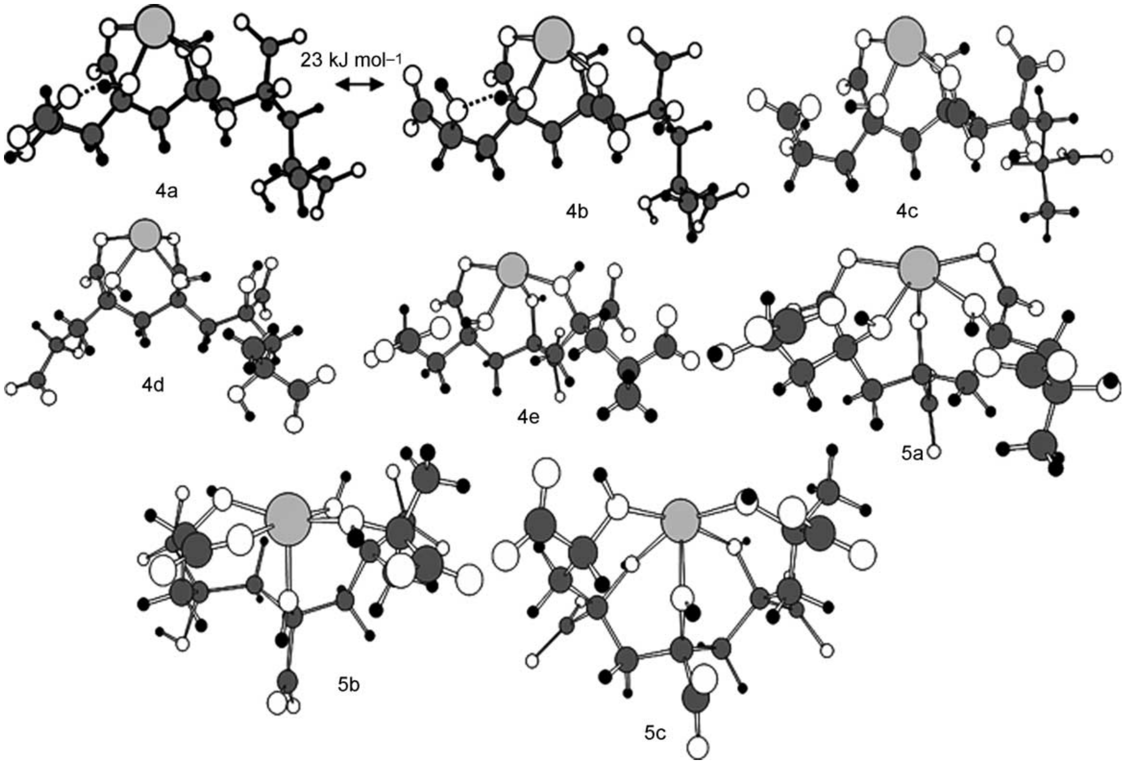

Fig. 5. Optimised geometries for 4- and 5-coordinated Mg^{2+}–PHA pentamer complexes (see Table 4 for energetics and caption of Fig. 2 for atom colours). The geometries for all other metals are similar with only minor differences in bond lengths and angles.

than five, we optimised PHA complexes with two ligands. These two ligands, both coordinating to the metal ion, were chosen to be a PHA dimer and a trimer for simply computational reasons. This situation was also considered to describe the circumstances where either a polymer chain forms a loose loop or two different polymer chains coordinate to the same metal ion.

The existence of two ligands with strong tendency for hydrogen bonding makes the configurational sampling of possible geometries far more demanding than in the case of one ligand. The observed sensitivity of the complexation energies to changes in hydrogen bonds makes proper configurational sampling even more important. However, as the presence of this kind of structures in solution is very probable and the local coordination mode is expected to be similar to pentamer-complexes, we found it both interesting and relevant to study this situation also.

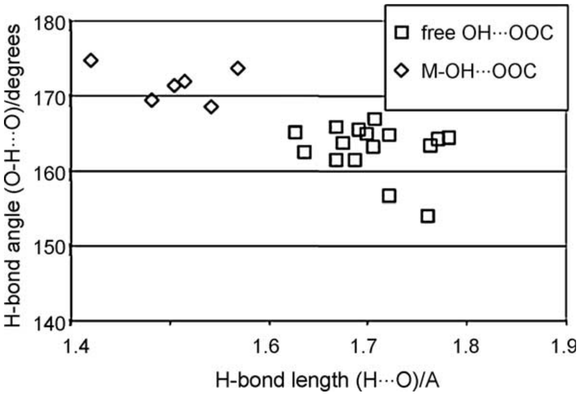

Fig. 6. The hydrogen bond angle (O···H–O/degrees) in PHA pentamer–metal structures as a function of hydrogen bond length (H···O/Ångströms).

Some of the optimised structures, their uncorrected and corrected complexation energies are shown in Table 5. The geometries of corresponding Ca^{2+} complexes are shown in Fig. 7. The energetically most favourable structure for all metal ions was a 6-coordinated geometry with three oxygen atoms from both COO^{-} and OH groups. As seen in Fig. 7, three 5-membered chelate rings are formed. Calcium was the only metal, which was found to have an 8-coordinated structure with these two ligands. This 8-coordinated structure, shown also in Fig. 7., was energetically only 5 kJ mol^{-1} less favourable than the 6-coordinated structure.

Complexation energies obtained with two PHA ligands are more than 25 kJ mol^{-1} less negative for all metals than for the PHA pentamer. This may indicate that a PHA polymer does not

Table 5

6- and 8-coordinated metal complexes of PHA dimer and trimer, their uncorrected and corrected complexation energies (in kJ mol^{-1})

Metal	Coordination number	O_{hyd}	ΔE_{csm} (kJ mol^{-1})	ΔG_{C2} (kJ mol^{-1})
Mg^{2+}	6	3	−64	27
Ca^{2+}	6	3	−62	15
Mn^{2+}	6	3	−97	18
Fe^{3+}	6	3	−265	19
Zn^{2+}	6	3	−111	5
Ca^{2+}	8	4	−57	20

O_{hyd} refer to the number of metal coordinating hydroxyl oxygen atoms.

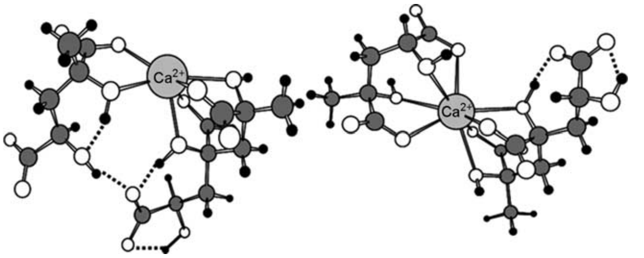

Fig. 7. Optimised geometries for 6- and 8-coordinated Ca^{2+}–PHA(dim + trim) complexes (see Table 6. for energetics). Hydrogen bonds are shown with dotted lines. The 6-coordinated geometries for all other metals are similar with only minor differences in bond lengths and angles (8-coordinated structure was found only for Ca^{2+}).

fill all the coordination positions of metal ions. Still, as the complexation energies were found to be very sensitive to changes in internal hydrogen bonds, there is no guarantee that the global minimum energy structure for dimer/trimer-type metal complexes was found, or that representing the polymer with these very short oligomers is sufficient. As mentioned earlier, the configurational sampling for complexes with two ligands is a very demanding task due to the strong intermolecular interaction between the ligands and, therefore, the results must be evaluated critically. Even so, the binding degree of PHA obtained by two ligands satisfy the experimentally obtained binding trends ($Zn^{2+} > Ca^{2+}$, $Ca^{2+} > Mn^{2+}$, $Ca^{2+} > Mg^{2+}$, $Zn^{2+} > Mn^{2+}$) [8] even better than in the case of one PHA pentamer ligand.

3.4.1.3. Metal complexes of PHA with explicit water molecules. As the minimum energy structures with PHA pentamer were found to have coordination number of four, we optimised the structure **4a** for all metal ions with two explicit water molecules. The coordination number of six for all metal ions was assumed. This assumption is reasonable since this is the most common coordination water number of metals we are studying [25].

Addition of explicit water molecules in the PHA-M-complexes did not alter the metal–ligand bonding pattern. The orientation of the explicit water molecules was found to be slightly disturbed from the octahedral starting structure so that they could form hydrogen bonds with the oxygen atoms from the carboxylate and hydroxyl groups of the ligand. This was seen also in our previous study [16] where the cluster-continuum approach (continuum solvation model together with explicit water molecules, respectively) was applied to the $[Ca–ISA]^{2-}$ complexes.

In order to further study the effect of explicit water molecules in the first solvation shell of the metal ions, we added one or two water molecules to the 6-coordinated structure of Ca^{2+} with PHA dimer and trimer ligands. The reason for this was to study the total coordination number of calcium ion, which varies between six and eight in aqueous environment. COSMO-optimised structures for these two metal complexes of Ca^{2+} are shown in the Fig. 8 together with their corrected complexation energies.

As seen in Fig. 8, the addition of one explicit water molecule to the 6-coordinated structure does not change the metal–ligand coordination geometry and thus, Ca^{2+} ion is 7-coordinated. However, the addition of two water molecules to the same structure causes a detachment of one hydroxyl oxygen atom and the added water molecule forms a hydrogen bond with detached hydroxyl oxygen atom and thus, Ca^{2+} prefers to remain 7-coordinated.

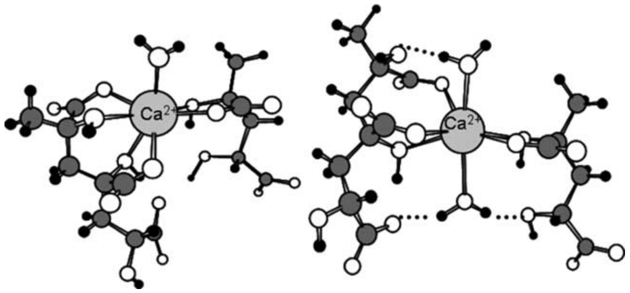

Fig. 8. Ca^{2+}–PHA(dim + trim)-complexes with explicit water molecules. Corrected complexation energies of complexes are 13 and 58 kJ mol^{-1}.

3.4.2. Metal complexes of PAA

In a deprotonated PAA pentamer, there are 10 possible metal-coordinating oxygen atoms. If we assume a monodentate coordination mode for a carboxylate group, the highest anticipated coordination number for a metal–ligand complex is five. Different configurations and coordination modes were studied as above. For some metal ions, e.g. Ca^{2+}, a bidentate coordination of a carboxylate group has been suggested on the grounds of crystal structure analysis [26]. This possibility of both carboxylate oxygen atoms to coordinate to metal ion was also studied. Since we did not find 5-coordinated PAA pentamer complexes, we employed also the dimer + trimer description of the polymer as above, in order to find structures with coordination number of five and, on the other hand, to model the situation where either the polymer forms a loose loop or two different polymer chains coordinate to the metal ion.

Some representative structures, their uncorrected and corrected complexation energies are shown in Table 6. Both the pentamer and dimer/trimer complexes of PAA are included in the table. The geometries of representative Fe^{3+} complexes are shown in Fig. 9.

With pentamer ligands the most favourable structure for all metal ions is 3-coordinated. With dimer and trimer ligands Mn^{2+} and Zn^{2+} favour a coordination number of four and for Mg^{2+}, Ca^{2+} and Fe^{3+}, the most favourable structure is 5-coordinated. Complexation energies for PAA pentamer complexes are significantly higher (more than 40 kJ mol^{-1} for all metal ions!) than those of PHA complexes. The dimer and trimer complexes, on the other hand, are energetically lower than corresponding PHA complexes (see Tables 4 and 5 for reference). Corrected complexation energies indicate that PAA is the most efficient binder for Zn^{2+}, Fe^{3+} and Mn^{2+} ions: complexation energies for Zn^{2+} and Fe^{3+} are even lower than in the case of a PHA pentamer ligand (see Table 4). The obtained binding degree ($Fe^{3+} > Zn^{2+} > Mn^{2+} > Ca^{2+} > Mg^{2+}$) is in good agreement with available experimental

Table 6
3-, 4- and 5-coordinated metal complexes of PAA, their uncorrected and corrected complexation energies (see Fig. 8 for the geometries and Fig. 9 for 2-coordinated complexes of Mg^{2+} and Ca^{2+})

Ligand	Metal	Coordination number	ΔEcsm (kJ mol^{-1})	ΔG_{C2} (kJ mol^{-1})
PAApenta	Mg^{2+}	3	−39	52
PAApenta	Ca^{2+}	3	−31	46
PAApenta	Mn^{2+}	3	−75	40
PAApenta	Fe^{3+}	3	−245	39
PAApenta	Zn^{2+}	3	−86	30
PAAdim+trim	Mg^{2+}	4	−67	24
PAAdim+trim	Ca^{2+}	4	−70	7
PAAdim+trim	Mn^{2+}	4	−122	−7
PAAdim+trim	Fe^{3+}	4	−299	−15
PAAdim+trim	Zn^{2+}	4	−139	−23
PAAdim+trim	Mg^{2+}	5	−77	14
PAAdim+trim	Ca^{2+}	5	−81	−4
PAAdim+trim	Mn^{2+}	5	−117	−2
PAAdim+trim	Fe^{3+}	5	−319	−35
PAAdim+trim	Zn^{2+}	5	−107	9

results of Sebastian et al. ($Fe^{3+} > Zn^{2+}$) [9] and Tamura et al. ($Ca^{2+} > Mg^{2+}$) [8].

The geometries of the most favourable Zn^{2+} and Fe^{3+} complexes are in good agreement with experimental results of Sebastian et al. [9] based on IR and UV measurements. They have suggested that Zn(II) favours tetrahedral geometry with PAA while Fe(III) complexes have an octahedral geometry. As seen in Table 6 and Fig. 9, the 4-coordinated tetrahedral structure with two PAA ligands is for Zn^{2+} energetically more than 30 kJ mol^{-1} lower than the 5-coordinated (distorted) octahedral geometry. This 5-coordinated octahedral geometry leaves one coordination site open (below the plane of paper in Fig. 9) which is very likely filled by a water molecule from the solution and thus completes the octahedral geometry. Fe^{3+}, in contrast, favours the 5-coordinated structure with an energy difference of 20 kJ mol^{-1}. Also, this structure has an open coordination site for a solvent molecule.

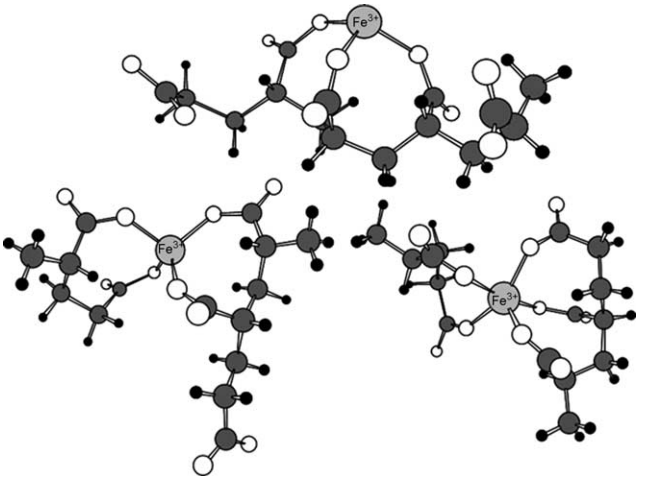

Fig. 9. Fig. 9 Optimised geometries for 3-, 4- and 5-coordinated complexes of Fe^{3+} with PAA pentamer and PAAdimer/trimer ligands. The geometries for all other metals are similar with only minor differences in bond lengths and angles.

‘Bidentate’ complexes where both carboxylate oxygen atoms coordinate to the metal ion were found only for Mg^{2+} and Ca^{2+} ions. Complexation in that fashion was found to be remarkably unfavourable for Mg^{2+} with a ΔG value of 70 kJ mol^{-1}. For Ca^{2+}, the ‘bidentate’ complex is only 5 kJ mol^{-1} higher than the 3-coordinated complex with a PAA pentamer. Geometries of these two ‘bidentate’ complexes are shown in Fig. 10 including M^{2+}–O-distances (in Ångströms) and O–C–O angles (in degrees).

Experimental results mostly based on analysis of crystal structures, imply that this ‘bidentate’ or ‘direct bonding’ is common with large metal ions with M–O distances of about 2.3–2.6 Å [26]. Unlike Mg^{2+}, Ca^{2+} falls into this category and thus the binding in that fashion is more favourable for Ca^{2+} than for metal ions with a smaller radius.

3.4.3. Comparison

The binding properties of PHA and PAA can be evaluated by comparing the obtained corrected complexation energies for different metals. Fig. 11 shows the corrected complexation energies for all metal–ligand-combinations.

Tamura et al. [8] have suggested, that the binding degrees of PHA and PAA for Ca^{2+} and Mg^{2+} decrease in the order PHA/Ca^{2+} > PAA/Ca^{2+} > PAA/Mg^{2+} > PHA/Mg^{2+}. According to our results, PHA seems to bind Mg^{2+} better than PAA with about 10 kJ mol^{-1}. The comparison of two different ligands with same metal is independent of correction parameters ($\tilde{G}_{ML_i}$) and, therefore, the results can be considered more reliable. PAA was found to be the most effective binder for Fe^{3+} and Zn^{2+} ions.

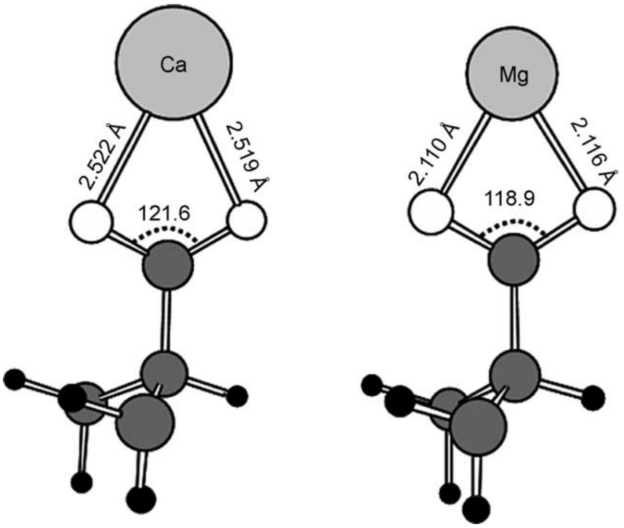

Fig. 10. Optimised geometries for bidentate complexes of Mg^{2+} (right) and Ca^{2+} (left) with a PAA pentamer. The binding monomer unit is the one in the middle of pentamer. Both ends of the oligomer are excluded in the figure for clarity. Corrected complexation energies of the complexes are 50 kJ mol^{-1} (Ca^{2+}) and 70 kJ mol^{-1} (Mg^{2+}), respectively. O–M bond lengths (in Ångströms) and O–C–O angles (in degrees) are also shown.

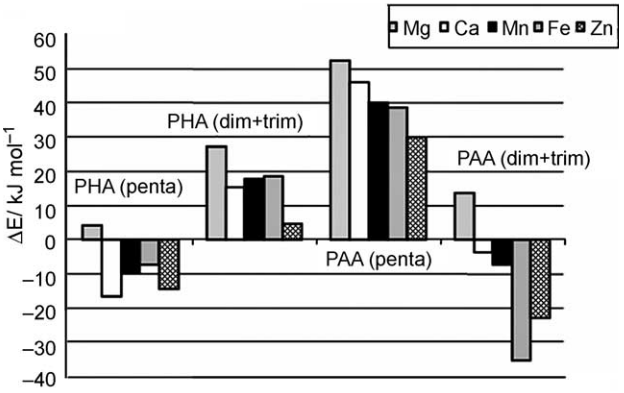

Fig. 11. Corrected complexation energies ΔE_{csm} for different metals with studied ligands (see Tables 4–6 for energetics and Figs. 5, 7 and 8 for geometries).

4. Discussion

Obtained binding trends are in good agreement with available experimental results. Minimum energy geometries are reasonable and we are quite convinced that the most favourable complexation geometries for each metal–ligand combination have been found. However, even if we find relative energies sufficient, the absolute energetics must be viewed with criticism. Also, because we model polymers with pentamers (or a dimer and a trimer), some aspects of the long polymers are not described well.

Metal specific correction parameters, $\tilde{G}_{\mathrm{ML}_i}$, have been determined with metal complexes of well-known (amino) polycarboxylic ligands [16]. An obvious and more accurate choice would have been to use one correction parameter for each metal and one for each ligand. However, this is not possible, since there exists no (accurate) thermodynamical data related to metal-polymer complexation. On the other hand, the differences in the ligand specific correction parameters used for the (amino)carboxylic acids are within 27 kJ mol^{-1} for seven different ligands, which suggests an upper bound for the error related to their omission.

Since in the present case, the ligands (oligomers) are rather similar, the ligand specific parameters have very likely same magnitude. It seems that the absolute values of the complexation energies are rather small with respect to the experimental observation of these polymers' capability to bind metals but the binding trends are in good agreement with available experimental results.

The complexation energy calculations with this approach do not include explicit thermal or internal entropy corrections. Also, corrections for ZPE, non-electrostatic solvation effects, and basis set superposition error (BSSE) are omitted. The accurate calculation of these contributions is both demanding and computationally expensive. Those terms (either some of them or all) have been successfully neglected in similar studies earlier [27]. Furthermore, as the aim of this study was to test this method for new ligands, our main concern is not the neglected contributions to complexation energies but the general performance and suitability of this method. In spite of neglected contributions, to our knowledge, this is the most sophisticated polymer–metal complexation study based on DFT up to date.

The oligomer ligands and their metal complexes have extremely many possible geometries. Studying all of them is, obviously, impossible. In this study, over 250 geometries were optimised, most of them being geometries of PHA and its complexes. This size of configurational sampling was possible only with the simplified energy expression, which omits the computationally expensive corrections mentioned above. We are quite convinced that we have found the most favourable structures for the metal-complexes of PHA. The addition of explicit water molecules was not found to change to metal-ligand bonding pattern except in the case of Ca^{2+}–PHA(dim + trim) type complex, where the detachment of one metal-coordinating hydroxyl oxygen atom appeared. However, it is well-know that the coordination number of Ca^{2+} varies between 6 and 8. The question is, how well our method, based on the BP86/COSMO-approach and the use of short oligomers as ligands, describes the circumstances and complexation properties of the real systems that we are studying.

The chemical composition of the mechanical pulp is very complicated. In addition to the complexating agent (polymer), there are lots of other possible metal-coordinating functional groups and thus, it is not evident that functional groups in polymers are the only groups participating in metal ion binding. Furthermore, the role of counter ions (Na^{+}) in complexation of di- or trivalent metal ions remains to be studied in the future. Nevertheless, as the modelling of the whole pulp system containing metal ions, polymers, and all the other substances is impossible at present, it is clear that one has to make some fundamental assumptions concerning the size and the level of theory for the system under study.

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 two polycarboxylic acid ligands, poly(α-hydroxy acrylic acid) (PHA) and poly(acrylic acid) (PAA). In addition to the free oligomers their complexes with Mg^{2+}, Ca^{2+}, Fe^{3+} and Mn^{2+} with PHA and PAA oligomers are reported.

The minimum energy geometries are reasonable, and they imply that the metal ions are not completely shielded by the ligands. Thus, the transition metals that catalytically decompose peroxides may still remain active, or they are shielded from the solvent by other mechanisms not seen with the small oligomers as polymer models. The addition of explicit water molecules to minimum energy structures was not found to have an effect on the metal–ligand bonding pattern and, therefore, we conclude that the continuum solvent description performs satisfactorily well in this case.

The obtained binding degrees are in good agreement with experimental results, even though the energy differences are small. In the case of PHA, the syndiotactic-binding site of the

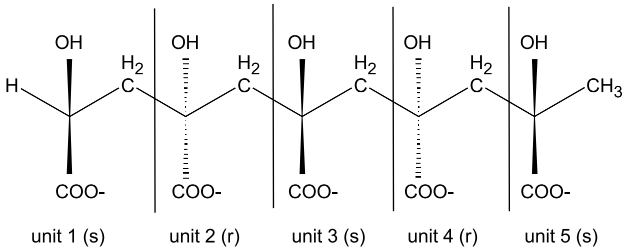

Fig. A1. Stereochemisty of PHA oligomers.

oligomer was found to be the most favourable one for complexation. The role of the OH group in metal ion binding was observed to be more important for Ca^{2+} than for other metals. Deprotonation of a metal-coordinating OH group was found to occur in the case of Fe^{3+}. For transition metal ions, especially for Fe^{3+} and Zn^{2+}, PAA was found to be the more effective binder. Also this supports the experimental observation that the role of OH groups is more significant in the case of Ca^{2+} than for transition metal ions.

It is evident that the pentamer structures do not describe all the binding properties of a polymer at satisfactory level and thus, further studies are needed, especially for understanding the longer polymers and the role of counter ions. However, to our knowledge, this is the first computational study related to complexation properties of polymers at this level of theory. The method developed in a previous study [16] and applied here is fast and straightforward. Its applicability for other ligands and its reliability will be further studied and tested in the future.

Acknowledgements

The authors wish to acknowledge CSC, the Center of Scientific Computing (Espoo, Finland) for the generous amount of computer time and software. Kemira Oyj is gratefully acknowledged for financial support.

Appendix

Stereochemistry of PHA oligomers

We have used the RS-methodology in the description of PHA oligomers stereochemistry. The monomer units are numbered according to Fig. A1. As we have terminated oligomers with hydrogen atoms, we have decided to give the lower priority always to the oligomer tail with monomer unit one and higher priority to the oligomer end with monomer unit five, respectively.

Structural information of metal complexes

The metal–oxygen distances in 4- and 6-coordinated structures of PHA metal complexes are shown in Table A1 (Refer to Tables 4 and 5 for energetics and Figs. 5 and 7 for

Table A1
Metal–oxygen distances (in Ångströms) in 4- and 6-coordinated PHA complexes

Complex	Metal	*d* (M–O1)	*d* (M–O2)	*d* (M–O3)	*d* (M–O4)	*d* (M–O5)	*d* (M–O6)	d_{exp}(M–O_{carb})
4a	Mg^{2+}	2.112	2.127	–	2.1	2.092	–	
4a	Ca^{2+}	2.500	2.482	–	2.467	2.464	–	
4a	Mn^{2+}	2.242	2.228	–	2.109	2.095	–	
4a	Fe^{3+}	1.975	1.978	–	2.048	2.034	–	
4a	Zn^{2+}	2.137	2.175	–	2.015	2.023	–	
6	Mg^{2+}	2.211	2.178	2.108	2.094	2.131	2.037	2.088
6	Ca^{2+}	2.557	2.501	2.511	2.465	2.468	2.411	2.39
6	Mn^{2+}	2.398	2.295	2.235	2.121	2.157	2.079	2.15
6	Fe^{3+}	2.233	2.172	2.07	1.987	2.018	1.949	2.00
6	Zn^{2+}	2.137	2.224	2.377	2.023	2.045	2.094	2.09

(See Tables 4 and 5 for energetics and Figs. 5 and 7 for geometries). O1, O2 and O3 are metal bonding hydroxyl oxygen atoms and O4, O5 and O6 carboxylate oxygen atoms. Experimental reference values for metal–carboxylate oxygen atom distances (d_{exp}(M–O_{carb})) taken from. Ref. [28].

Table A2
Metal–oxygen distances (in Ångströms) in 4-, and 5-coordinated PAA complexes

Complex	Metal	*d* (M–O1)	*d* (M–O2)	*d* (M–O3)	*d* (M–O4)	*d* (M–O5)
4	Mg^{2+}	1.981	1.987	1.983	1.963	–
4	Ca^{2+}	2.380	2.373	2.396	2.359	–
4	Mn^{2+}	2.048	2.044	2.045	2.020	–
4	Fe^{3+}	1.903	1.908	1.900	1.884	–
4	Zn^{3+}	1.996	1.990	1.979	1.967	–
5	Mg^{2+}	2.085	2.037	2.059	2.040	2.089
5	Ca^{2+}	2.370	2.399	2.389	2.394	2.395
5	Mn^{2+}	2.115	2.152	2.109	2.147	2.132
5	Fe^{3+}	2.006	1.986	1.992	2.006	1.944
5	Zn^{2+}	2.086	2.074	2.114	2.083	2.029

(See Table 6 for energetics and Fig. 8 for geometries). O1 and O2 are metal bonding carboxylate oxygen atoms from dimer, O3, O4 and O5 from trimer, respectively.

geometries). As a reference value, the carboxylate oxygen–metal distance from the Ref. [28] is shown (see also average metal–oxygen distances for hexahydrates, Table 2).

Table A1 shows that for all metals (except for Fe^{3+}-complex **4a**), M–$O_{carboxylate}$ distances are shorter than those for M–$O_{hydroxyl}$. For Mg^{2+} and Ca^{2+}M–O distances are slightly larger than the reference values. For transition metals, on the other hand, values are smaller than the reference values. As seen in Table A2, for the metal complexes of PAA, transition metal–carboxylate oxygen bonds are even stronger than in complexes of PHA.

References

[1] Roth JA, Garrick MD. Biochem Pharmacol 2003;66:1.
[2] Yang Z, D'Entremont M, Ni Y, Heiningen ARP. Pulp Pap Can 1997;11: T408.
[3] Sillanpää M. Rev Environ Contam Toxicol 1997;152:85. Sykora V, Pitter P, Bittnerova I, Lederer T. Water Res 2001;35(8):2010. Sillanpää M, Pirkanniemi K. Environ Technol 2001;22:791.
[4] Tamura T, Uehara H, Ogawara K, Kawauchi S, Satoh M, Komiyama J. J Polym Sci, Part B: Polym Phys 1999;37:1523.
[5] Kotin L, Nagasawa M. J Chem Phys 1962;36:873.
[6] Kawaguchi S, Kitano T, Ito K, Minakata A. Macromolecules 1990;23:731.
[7] Davenport JN, Wright PV. Polymer 1983;21:287. Towlson M, Wright PV. Polym Commun 1983;24:79.
[8] Tamura T, Kawabata N, Kawauchi S, Satoh M, Komiyama J. Polym Int 1998;46:353.
[9] Sebastian N, George B, Mathew B. Polym Degrad Stab 1998;60:371.
[10] Yamazawa K, Kawauchi S, Satoh M. J Polym Sci, Part B: Polym Phys 2002;(40):1400.
[11] Tamura T, Kawabata N, Satoh M. Polym Bull 2000;44:209. Tamura T, Yoshida S, Miyamoto Y, Kawauchi S, Satoh M, Komiyma J. Polym Int 2000;49:147.
[12] Tamura T, Kawauchi S, Satoh M, Komiyama J. Polymer 1998;39:1555–8.
[13] Tamura T, Kawauchi S, Satoh M, Komiyama J. Polymer 1997;38:2093.
[14] Christensen JJ, Eatough DJ, Izatt RM. Chem Rev 1974;74:351.
[15] Buhl M, Wipff G. J Am Chem Soc 2002;124:4473. Moore MB, Ray D, Armentrout PB. J Am Chem Soc 1999;121:417.
[16] Sillanpää AJ, Aksela R, Laasonen K. Phys Chem Chem Phys 2003;5: 3382.
[17] Ahlrichs R, Bär M, Häser M, Horn H, Kölmel C. Chem Phys Lett 1989; 162:165.
[18] Becke AD. Phys Rev A 1988;38:3098. Perdew J. Phys Rev B 1986;33: 8822.
[19] Eichkorn K, Treutler O, Öhm H, Häser M, Ahlrichs R. Chem Phys Lett 1995;240:283. Eichkorn K, Treutler O, Öhm H, Häser M, Ahlrichs R. Chem Phys Lett 1995;242:252.
[20] Klamt A, Schüürmann G. J Chem Soc Perkin Trans 1993;2:799.
[21] Koch W, Holthausen MCA. Chemist's guide to density functional theory. New York, NY: Wiley-VHC; 2000.
[22] Burgess J. Metal ions in solution. New York, NY: Wiley; 1978.
[23] Ogawara K, Kawazoe S, Tamura T, Kawauchi S, Satoh M, Komiyama J. Polymer 1998;39:437.
[24] Strouse J, Layten SW, Strouse CE. J Am Chem Soc 1977;99(2):562. Strouse J. J Am Chem Soc 1977;99(2):572.
[25] Ohtaki H, Radnai J. Chem. Rev. 1993;93:1157.
[26] Katz AK, Glusker JP, Beebe SA, Bock SW. J Am Chem Soc 1996;118: 5752. Carrell CJ, Carell HL, Erlebacher J, Glusker JP. J Am Chem Soc 1998;110:8651. Katz AK, Glusker JP, Markham GG, Bock CW. J Phys Chem B 1998;102:6342.
[27] Martin RL, Hay PJ, Lawrence RP. J Phys Chem A 1998;102:3565. Pliego JR, Riveros JM. J Phys Chem A 2001;105:7241. Cosentino U, Villa A, Pitea D, Moro G, Barone V. J Phys Chem B 2000;104:8001.
[28] Hocking RK, Hambley TW. Inorg Chem 2003;42:2833.