Outer-Sphere Hydration and Liquid−Liquid Partition of Metal(III) Chelates − Density Functional Calculations

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Hydration of two coordinatively saturated metal chelates, tris(propane-1,3-dionato)scandium(III) and tris(propane-1,3-dionato)cobalt(III), was studied theoretically using the density functional method with a three-parameter B3LYP implementation at different variants for calculating the hydration energy, including corrections for ZPVE, BSSE, polarisation functions, temperature and the number of hydrating water molecules in the system. Formation of hydrates was demonstrated, with water hydrogen-bonded to ligands (outer-sphere hydration). After corrections for side effects, good correlations were found between the energy and the length of these hydrogen bonds in the hydrates of both chelates. Also, the calculated changes in charge distribution on the atoms of hydrogen-bonded water in these model chelates qualitatively agree with the experimental ^{1}H NMR spectroscopic data for the analogous tris(pentane-2,4-dionato)cobalt(III) species. An implicit solvation model (SCI-PCM) was used to take into account solvent effects of water and heptane on the energies of the model chelates studied and to calculate their enthalpies of transfer from heptane to water. In spite of simplifications in the model, satisfactory agreement was found between the calculated values and the experimental standard enthalpies of transfer of the analogous chelates, namely the tris(pentane-2,4-dionates) of scandium and cobalt(III).

Introduction

Interactions between amphiphilic molecules and water play an important role in numerous chemical and biochemical processes. References cited in ref.[1] are devoted to theoretical studies on hydrogen bonding in systems consisting of relatively simple molecules. Theoretical chemistry well describes simple hydrogen bonded systems composed of two small molecules.[2] On the other hand, large hydrogen-bonded structures are of greater interest not only because of their chemical complexity but also due to their practical importance. Theoretical calculations make it possible to quantify hydrogen-bonding interactions in large supermolecular systems with light atoms (organic species), not only in vacuo but also in solvent-modelling environments.[3] Less common are theoretical studies on hydrogen bonding in metal complexes. Because of computational problems, investigations on such systems develop rather slowly, although fast and efficient methods based on density functional theory (DFT), supplemented by using polarisation functions, have been successfully applied to solve various chemical problems dealing with *d*- and *f*-electron metal ions.[4−8] DFT calculations were used to study the effect of hydrogen bonding between solvent molecules and ligands on the stability of copper(I) thiocyanate complexes. However, scarce information is available on the calculation details.[9] More informative in this context are extensive theoretical studies on the hydrogen bonding of various proton donors to metal hydrides.[10]

With only moderate success gained from theory, experimental methods still predominate in studying large hydrogen-bonded, metal containing structures. From the numerous problems intensively studied in this field, we have focussed on the interactions of amphiphilic metal chelates with solvent water. Hydrogen bonding is responsible for two effects observed in aqueous solutions of the chelates: (1) Hydrophobic hydration which makes the thermodynamic activity of the solute (chelate molecule) higher because of promotion of the local structure of water around the hydrocarbon fragments of ligands, resulting from hydrogen bonding between neighbouring water molecules and (2) outer-sphere hydration of metal chelates, i.e. hydrogen bonding of water molecules to hydrophilic fragments of coordinated ligands, in particular to electron-donor oxygen atoms that coordinate to the central metal ion. The latter process, resulting in a decrease in the thermodynamic activity of the

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solute, has been observed and comprehensively studied in a series of experimental studies by our group.[11]

All these aqueous-phase interactions influence liquid−liquid partition of metal chelates and play an important role in solvent extraction of metal ions. Unfortunately, as shown in our recent review,[12] many researchers who studied solvent extraction processes by computational modelling, focused their attention on the complex formation step and neglected hydration phenomena. The aims of the present work were: (1) To point out importance of the outer-sphere hydration, by supplying theoretical evidence for hydrogen bonding between molecules of water and coordinatively saturated metal chelates, (2) to reproduce properties of these hydrogen-bonded systems in terms of energy and (3) to evaluate the effects of various calculation approaches, including models, basis sets, polarisation functions and temperature, etc on the reliability of the calculation results.

A supermolecular approach[13] was used in this work which assumes formation of molecular adducts, i.e. the outer-sphere hydrates of metal chelates. Model molecules were studied with a fewer number of ligand CH_2 groups than in real chelates. Apart from the energies of adduct formation in the gas phase, standard enthalpies of transfer (heptane → water) of the model molecules were calculated and compared with experimental data for two coordinatively saturated metal acetylacetonates. Therefore, solvent effects were included in the calculations by modelling both liquid phases (heptane and water) with continuous electrostatic fields which surrounded the molecules studied. In the next section, various approaches used for the calculation of total energies of all the species studied after optimisation of their structures in the gas phase are presented.

Calculation Method

Let us assume that two molecules, X and HY, form a hydrogen-bonded adduct (hydrate) X···HY, accompanied by some deformation of the original molecules. The relative positions of X and HY in the hydrate can be described by the system of intermolecular coordinates, R. The internal coordinates of X and HY in the hydrate, r_X and r_{HY}, differ from the respective equilibrium values in the free molecules, r_Xf and r_{HY}f. According to the supermolecular approach, a fundamental formula for the energy of interaction (at 0 K) between X and HY is:

$$E_{\mathrm{int}} = E_{\mathrm{XHY}}(R,r_{\mathrm{X}}, r_{\mathrm{HY}}) - E_{\mathrm{X}}(r_{\mathrm{X}}\mathrm{f}) - E_{\mathrm{HY}}(r_{\mathrm{HY}}\mathrm{f}) + \Delta\mathrm{ZPVE} \qquad (1)$$

where $E_{XHY}(R,r_X,r_{HY})$ is the total energy of the hydrate and $E_X(r_Xf)$ and $E_{HY}(r_{HY}f)$ are the total energies of the chelate and water molecules (fully optimised). The E_{int} value must be corrected for the difference between the zero-point vibrational energies (ZPVE − energy of molecular vibrations at 0 K) of the hydrate and its free components, ΔZPVE. If polarisation functions are included in the basis sets used, we denote the energies with *, e.g. E^*_{int}.

Because Equation (1) overestimates the intermolecular attraction, the interaction energy in weakly bound supermolecules should be corrected for the basis set superposition error (BSSE). We applied the counterpoise procedure described by Boys and Bernardi[14] and calculated total energies of the X and HY molecules in the hydrate geometry and in the hydrate basis set: $E_{X(HY)}(R,r_X,r_{HY})$ and $E_{HY(X)}(R,r_X,r_{HY})$:

$$E^0_{\mathrm{int.}} = E_{\mathrm{XHY}}(R,r_{\mathrm{X}},r_{\mathrm{HY}}) - E_{\mathrm{X(HY)}}(R,r_{\mathrm{X}},r_{\mathrm{HY}}) - E_{\mathrm{HY(X)}}(R,r_{\mathrm{X}},r_{\mathrm{HY}}) + \Delta\mathrm{ZPVE} \qquad (2)$$

In many systems this correction, BSSE = $E^0_{int} - E_{int}$, is larger than the energy difference which results from the Born-Oppenheimer approximation and from neglecting anharmonicity.

The calculations [Equations (1)−(2)] refer to 0 K. In order to predict the energy of the system at a nonzero temperature T, terms for a thermal energy correction must be added to the total energies, i.e. E_A (A = XHY, HY, or X) which includes the effects of molecular vibration $E_{A,vib}$, rotation $E_{A,rot}$ and translation $E_{A,transl}$:

$$E^{\mathrm{T}}_{\mathrm{A}} = E_{\mathrm{A}} + E_{\mathrm{A,vib}} + E_{\mathrm{A,rot}} + E_{\mathrm{A,transl}} \qquad (3)$$

The energy of interaction can then be calculated without the zero-point correction:

$$E^{\mathrm{T}}_{\mathrm{int.}} = E^{\mathrm{T}}_{\mathrm{XHY}} - E^{\mathrm{T}}_{\mathrm{X}} - E^{\mathrm{T}}_{\mathrm{HY}} \qquad (4)$$

All the energies calculated for the gas phase are not directly comparable with the experimental data which refer to the process of the chelate transfer from heptane to water. To make such a comparison plausible, solvent effects of the liquid environment on the solute energy must be taken into account in the calculations, e.g. by use of a Self-Consistent Isodensity Polarised Continuum Model (SCI-PCM).[15] This procedure locates the solute molecule within a cavity formed in the field with the dielectric constant of a given liquid, either water ($\varepsilon_w = 78.3$) or heptane ($\varepsilon_h = 1.92$), and then the electron density is determined which minimises the energy of the whole system. The optimised gas-phase structures of all the species (hydrate, chelate and water molecules) were used.

From the thermodynamic point of view, the process of aqueous-phase hydration of a solute molecule (e.g. metal chelate) originally present in another phase (e.g. heptane) can be divided into two steps: (1) Transfer of the chelate molecule to the aqueous solution, followed by (2) addition of water molecule(s) present in bulk water to the chelate by, for example, hydrogen bonding, i.e. formation of a supermolecule (hydrate) in the aqueous phase. The energy change (at 0 K) corresponding to formation of the 1:1 adduct is

$$E_{h-w} = E_{XHY}(w) - E_X(h) - E_{HY}(w) + \Delta ZPVE \qquad (5)$$

where the total energies of the molecules (defined by the indexes) are calculated in the field of either water (w) or heptane (h). Assuming that the small temperature correction, $\Delta E^T = E^T_{int.} - E_{int}$, does not depend on the environment, the energy change at temperature T is equal to $E^T_{h-w} = E_{h-w} + \Delta E^T$ and (with the definition $H^T_A = E^T_A + RT$) the enthalpy change for the 1:1 adduct formation is $\Delta H^T_{h-w} = E^T_{h-w} - RT$. The same also holds for the 1:3 adduct, assuming that one of its components is a single molecule of a water trimer.

The calculations were first carried out in the model systems consisting of a molecule of water and a molecule of the metal chelate, i.e. $M(mala)_3$ = tris(propane-1,3-dionato)scandium(III) or tris(propane-1,3-dionato)cobalt(III). The ligand was a deprotonated enol form of malonaldehyde, $[O{=}CH{-}CH{=}CH{-}O]^-$, abbreviated as $mala^-$, which we assumed to be a suitable model for the pentane-2,4-dionate (acetylacetonate) anion. The metal ions scandium and cobalt(III) were selected for this study because their tris(acetylacetonates), $M(acac)_3$, have been experimentally[11d,11c] characterised as having the highest and the lowest standard enthalpies of transfer (see Table 5) within the whole series of 3d metal(III) ions. In other calculation systems, more water molecules were then used (see below). In all cases, the addition of water molecule(s) to the chelates resulted in the formation of the water adducts, either $M(mala)_3{\cdot}H_2O$ or $M(mala)_3{\cdot}3H_2O$, further referred to as hydrates.

The present calculations were based on the Density Functional Theory (DFT),[16] using the Lanl2dz double-ζ basis set[17] and the three-parameter Becke functionals of the B3LYP[18] type. The Berny geometry-optimisation algorithm[19] was applied to calculate the geometries of the neutral metal chelates, water and its multimers, as well as the 1:1 and 1:3 hydrates. The system Hessian with $(3n-6)$ eigenvalues confirms that the minimum energies were found for all the compounds. The calculations have also been performed with the use of the Huzinaga polarisation functions on each atom.[20] All the calculations were carried out by means of the Gaussian 94 package[21] using Cray J90 and Cray Y-MP supercomputers.

Results and Discussion

Geometry and Charge Distribution

Table 1 shows some selected B3LYP geometrical parameters of the model chelate molecules [distorted octahedral $Sc(mala)_3$ and $Co(mala)_3$] in the gas phase and the charge distributions on some of their atoms. The geometries mirror the experimental data for their crystalline analogues, $Sc(acac)_3$ and $Co(acac)_3$, within an acceptable error. The calculated M−O distances are somewhat shorter (by 0.02 - 0.03 Å). This is in accordance with the temperature difference (room temp. vs. 0 K for the calculations) and with the difference in the structure of the ligands, i.e. lack of two electron-releasing methyl groups in each $mala^-$ ligand in comparison with $acac^-$. The much larger span of the calculated atomic charges on Sc−O compared with Co-O (Table 1) can be interpreted in terms of a stronger covalent nature of the Co−O bond. The full set of calculation data for all components studied, including the hydrates (see below), is given in the Supporting Information (Table 8; for Supporting Information see also the footnote on the first page of this article).

The interaction between water and the metal chelates leads to formation of the adducts (hydrates) which can be considered to be supermolecules. Theoretical calculations of the structures of these adducts were carried out by minimising the energy of systems consisting of one molecule of a given chelate and one (or more) water molecule(s) in the gas phase (vacuum). The initial position(s) of the water molecule(s), i.e. the initial distance between the central metal ion M and the oxygen atom of water (or of a water molecule in a cyclic multimer), O_w, was varied. For the 1:1 adducts, three different cases were considered: (1) $d(M-O_w) < 2.5$ Å, the water molecule would be expected to coordinate directly to the M^{3+} ion by means of a lone electron pair on the O_w atom, thus increasing the coordination number (CN) of M^{3+}. This model corresponds to the inner-sphere hydration of the chelate. Optimisation of such a structure led to strong deformations and eventually "decomposition" of the water molecule which is inconsistent with the experiments on tris(acetylacetonates) of scandium[11d] and cobalt(III).[11c] This result confirms our basic assumption that the chelates studied are coordinatively saturated. (2) $d(M-O_w) > 4.5$ Å, the water molecule approached the CH groups or π-electrons of the ligand,

Table 1. Selected geometrical parameters of $M(mala)_3$ chelates in the gas phase and charge distributions on some of their atoms after DFT-B3LYP optimisation, and experimental structural parameters for crystalline $M(acac)_3$ chelates

Chelate	State	$d(M-O)$ (Å)	Bite angle (°)[a]	$q(M)$	$q(O)$ av.	Reference
$Sc(mala)_3$	gas	2.093	80.6	1.320	−0.445	this work
$Co(mala)_3$	gas	1.913	96.8	0.328	−0.289	this work
$Sc(acac)_3$	cryst.	2.070(9)	81.5(2) −82.3(2)	–	–	[22]
$Co(acac)_3$	cryst.	1.888(4)	96.2(2) −96.7(2)	–	–	[23]

[a] The angle O−M−O, both O atoms belonging to the same ligand.

weakly interacting with them. However, the total energy of such systems was rather high, therefore this was not the case of interest. (3) 4.0 Å $< d(M-O_w) <$ 4.5 Å, the system attained the lowest energy. The water molecule formed a hydrogen bond with one of the oxygen atoms of a ligand in the $M(mala)_3$ molecule. The reliability of our model of the outer-sphere hydration of the chelates has been confirmed this way. Additional calculations of the second derivatives of the energies for $Sc(mala)_3 - H_2O$ and $Co(mala)_3 - H_2O$ systems confirmed that the true energy minimum was attained. The optimised structure of the $Co(mala)_3{\cdot}H_2O$ adduct in the gas phase is given in Figure 1.

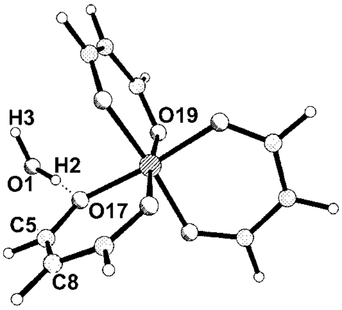

Figure 1. The optimised gas-phase structure of monohydrate $Co(mala)_3{\cdot}H_2O$. The metal ion occupies the central position. The other atoms mentioned in the text are numbered. Full numbering is given in the Supporting Information (Figure 8.2). The hydrogen bond between the water molecule and a ligand oxygen atom is shown by a dotted line.

Table 2 shows some selected geometrical parameters of the 1:1 hydrates and the changes in the charge distribution on selected atoms due to the hydrate formation. In both hydrates the oxygen atom of the water molecule is located at a short distance (ca. 2.8 Å typical for hydrogen bonding) from one of the oxygen atoms (O17 – For numbering of atoms in the hydrates see Figure 1 and Figure 2 and also Supporting Information, Figures 8.2 and 8.3) of a $mala^-$ ligand. The angles α (O1−H2−O17), β (O1−O17−C5) and γ (C8−C5−O17−O1) deviate slightly (by less than 10°-20°) from the expected values (sp^2 hybridisation of the ligand oxygen atoms was assumed): 180°, 120° and 180°, respectively. This shows that the hydrogen bond O1−O17 is nearly linear and only slightly deviates from the direction of the lone electron pair on the O17 atom. The small difference between O1−O17 distances in $Co(mala)_3{\cdot}H_2O$ and in $Sc(mala)_3{\cdot}H_2O$ points to a stronger hydrogen bond in the former hydrate, in spite of much less negative charge on the oxygen atoms in $Co(mala)_3$ than that in $Sc(mala)_3$ (Table 1). The electrostatic model of hydrogen bonding is, therefore, inapplicable for the hydrates studied.

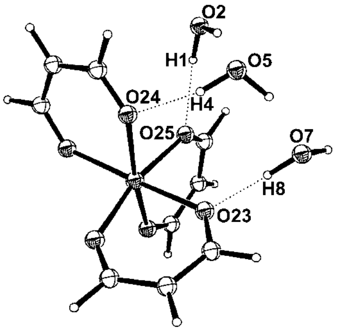

Figure 2. The optimised gas-phase structure of the trihydrate $Sc(mala)_3{\cdot}3H_2O$. The metal ion occupies the central position. The other atoms mentioned in the text are numbered. Full numbering is given in the Supporting Information (Figure 8.3). The hydrogen bonds between water molecules and ligand oxygen atoms are shown by dotted lines.

Table 2. DFT-B3LYP optimisation of monohydrates $M(mala)_3{\cdot}H_2O$ in the gas phase: Selected geometrical parameters, changes of charge distribution on selected atoms in the chelates upon hydrate formation (the numbering of indicated atoms is given in Figure 1)

M	Distances (Å)		Bond angles[a] (°)			Charge distribution changes on some atoms[b]					
	O1−O17	O1−O19	α	β	γ	M	O17	O19	H2	O1	H3
Sc	2. 806	3.244	171.1	111.5	175.2	−0.012	−0.060	−0.014	+0.074	−0.050	−0.008
Co	2.799	3.501	160.1	110.5	170.1	+0.009	−0.086	−0.003	+0.068	−0.042	−0.015

[a] The angles are: α = O1−H2−O17; β = O1−O17−C5; γ = C8−C5−O17−O1. [b] The charge change, Δq, is the difference between the atom charge in a given hydrate and in the respective chelate or water, calculated using Mulliken population analysis.

Table 3. DFT-B3LYP optimisation of trihydrates $M(mala)_3{\cdot}3H_2O$ in the gas phase: selected geometrical parameters and changes in charge distribution on selected atoms upon hydrate formation (the numbering of indicated atoms is given in Figure 2).

M	Hydrogen bond lengths (Å)					Water bond angles[a]	Charge distribution changes, Δq			
	O2−O25	O5−O24	O7-23	O2−O7	O5−O7		M	O_{ch}[b]	H_w [b]	O_w [b]
Sc	3.003	2.918	2.693	2.748	2.711	158	−0.030	−0.059	+0.023	+0.010
Co	2.949	2.874	2.759	2.847	2.829	160	+0.022	−0.087	+0.023	+0.018

[a] Average angles between the O−H bonds in the three hydrating water molecules (°). [b] Average changes in charge distribution on selected atoms: oxygens in the water molecules (O_w = O2, O5 and O7); the hydrogens in the water molecules participating in hydrogen bonding (H_w = H1, H4 and H8) and the oxygens in the chelate molecules participating in hydrogen bonding (O_{ch} = O25, O24 and O23). Δq is defined in Table 2.

Formation of the $M(mala)_3 \cdot nH_2O$ adducts is accompanied by small changes in the geometries of the original molecules and in the charge distributions on their atoms (Table 2 and Table 3, as well as Table 8 in Supporting Information). For example, in the 1:1 adducts, the Sc−O17 distance increases by about 0.03 Å, while the Co-O17 distance increases only by 0.004 Å. This difference may be explained in terms of a stronger covalency and greater strength of the Co−O bond compared with the Sc−O distance. The other M−O distances remain practically unchanged. In both systems the O1−H2 distances increase by about 0.01 Å and the angles H3−O1−H2 slightly decrease. The electron densities increase on the hydrogen-bonded oxygen atoms (O17, O1) and decrease on the hydrogen (H2). The summed-up decrease in the electron density on all hydrogen atoms of water in the hydrates is consistent with the significant downfield shift of the water proton resonance observed in the ^1H NMR spectrum of the $Co(acac)_3$ solution.[11b] All the results give us a picture of the hydrogen bonded systems which is in accordance with the hypothesis of outer-sphere hydration of metal chelates, based on the earlier experiments.[11]

Quite surprisingly, the analysis of the geometries of the hydrates has shown that apart from the expected hydrogen bond between the water molecule and a donor oxygen atom in the ligand of each chelate, an additional hydrogen bond has been detected in the scandium (but not the cobalt) hydrate. The relatively short O1−O19 distance in $Sc(mala)_3 \cdot H_2O$, equal to 3.24 Å, can be considered as evidence for a very weak hydrogen bond between the water molecule and another ligand in the chelate. The corresponding distance of 3.50 Å in $Co(mala)_3 \cdot H_2O$ is too long for hydrogen bonding. This additional interaction may explain why the total decrease in the electron density on the whole hydrogen bonded water molecule is larger in $Sc(mala)_3 \cdot H_2O$ ($\Delta q = +0.016$) than in $Co(mala)_3 \cdot H_2O$ ($\Delta q = +0.011$).

Since each chelate molecule in question has more than one hydrophilic site, we also studied its hydration taking into account more than one water molecule. Earlier semiempirical and ab initio calculations have shown that the lowest energy of a system consisting of a number of H_2O molecules in the gas phase is attained when the water molecules form cyclic multimers.[24,25] We have optimised the structures of the cyclic multimers consisting of three, six and nine H_2O molecules. After placing each multimer close to the chelate molecule [4.0 Å < d(M-O$_w$) < 4.5 Å, where O$_w$ denotes one of the oxygen atoms in the multimer], the systems were optimised again until the global minimum for each system (hydrate) was attained. Full optimisation of the 1:3 hydrates resulted in strong structural changes in the cyclic water trimer, i.e. breaking one of its hydrogen bonds, stretching the resultant chain and attaching it by means of hydrogen bonding to three oxygen atoms in the three mala ligands (Figure 2).

These structural changes may be considered to be a template effect. Optimisation of the systems with the water hexamer and nonamer led to formation of the 1:3 hydrate as well. The remaining water molecules were separated from the hydrate and moved away.

Table 3 shows some selected geometrical parameters (B3LYP) of the 1:3 hydrates and changes in the charge distributions on chosen atoms due to the hydrogen bonding. The average length of hydrogen bonds formed between the water molecules and the three mala ligands is somewhat shorter in $Co(mala)_3 \cdot 3H_2O$ (2.86 Å) than in $Sc(mala)_3 \cdot 3H_2O$ (2.87 Å) although the difference is small. In contrast, the deformation of the original water trimer is much stronger in the former hydrate. This is evidenced by longer distances between the neighbouring oxygens in the trimer chain in $Co(mala)_3 \cdot 3H_2O$ than in $Sc(mala)_3 \cdot 3H_2O$, 2.84 Å versus 2.73 Å on average. Both distances have significantly increased from the original 2.58 Å calculated for the cyclic water trimer (see Supporting Information, Table 8.5).

The summed-up decrease in the electron density on the three hydrogen bonded water molecules is greater in $Sc(mala)_3 \cdot 3H_2O$ ($\Delta q = +0.051$) than in $Co(mala)_3 \cdot 3H_2O$ ($\Delta q = +0.030$). This agrees very well with the respective changes on the single water molecules in the corresponding monohydrates, which are three times less (see above).

Energy of Hydrogen Bonding

The next challenge was to explain, at least at a model level, a possible reason for the stronger hydration (in aqueous solution) of $Co(acac)_3$ compared with $Sc(acac)_3$,[11d] something which was unexpected from the viewpoint of the electrostatic model of hydrogen bonding (see above). Therefore, the energy of hydrogen bonding between $M(mala)_3$ and water molecule(s) was calculated. It was assumed to be

Table 4. Energies of hydrogen bonding in the $M(mala)_3 \cdot nH_2O$ hydrates in the gas phase, X [kJ·mol^{-1}], calculated (DFT-B3LYP) in various variants

n	T, K	X	X_{Sc}/X_{Sc}^{cor} [a]	X_{Co}	$\Delta X_{Sc/Co}$[b]	X^*_{Sc}/X_{Sc}^{cor} [a,c]	X^*_{Co}[c]	$\Delta X^*_{Sc/Co}$[b,c]
1	0	E_{int}	−27.4/−18.7	−23.8	−3.6/+5.1	−18.3/−12.4	−16.9	−1.4/+4.5
1	0	E_{int}^{0}	−18.1/−9.4	−13.3	−4.8/+3.9	−11.6/−4.7	−8.1	−3.5/+3.4
1	298	E_{int}^{T}[d]	−26.5/−17.8	−22.5	−4.0/+4.7	−17.4/−11.5	−15.6	−1.8/+4.1
1	0	E_{int} − ZPVE[d]	−35.4	−31.2	−4.2	−26.3	−24.3	−2.0
3	0	E_{int} − ZPVE[d]	−26.1	−23.7	−2.4	−28.7	−26.7	−2.0

[a] $X_{Sc}^{cor} = E_{HB} = E_{int} - E_{HB}'$. $E_{HB}' = -8.7$ kJ·mol^{-1} (for X_{Sc}) or -5.9 kJ·mol^{-1} (for X^*_{Sc}). [b] $X_{Sc} - X_{Co}$ or $X_{Sc} - X_{Co}$ /$X_{Sc}^{cor} - X_{Co}$. [c] X^* values calculated with the use of polarisation functions. [d] For the values of ΔZPVE and temperature corrections see Supporting information, Table 6b.

the energy of interaction between the given molecules in the gas phase at 0 K (Table 4).

Since the DFT method takes into consideration a significant part of the electron correlation energy,[26] we could expect high accuracy and reliability from the calculations. Furthermore, the method was verified based on the comparison of the results obtained by the density functional calculations (using BLYP and BP functionals) with the exact solution of the Schrödinger equation for the helium atom in a model of harmonic interactions (Hooke model). Within the BLYP functional, the error in the total energy amounted to 0.87%, which was a half the error resulting from the Hartree−Fock method, while the BP functional energy error was only 0.08%.[27] This means that the DFT method with various correlation potentials is quite effective.

For the 1:1 hydrates the calculations were carried out in different variants, including (or not) corrections for the BSSE, ZPVE and temperature using (or not) the polarisation functions on each atom. Corrections for BSSE made the results even worse. An improvement was obtained using calculations with the polarisation functions. The temperature corrections gave negligible effects. On the other hand, a correction for the energy of the additional H-bond in $Sc(mala)_3{\cdot}H_2O$ (see above) appeared to be very important. This was calculated as the difference between the total energy of the optimised $Sc(mala)_3{\cdot}H_2O$ molecule, E_{XHY}, and the total energy of the same molecule with a somewhat distorted geometry, E_{XHY}', i.e. where the water molecule was twisted around the O1−O17 axis enough to break this additional bond but keeping unchanged all other important interactions, in particular the length of the main (O1−O17) hydrogen bond. The magnitude of this correction, E_{HB}', depended on the calculation variant (see Table 4−5 and Supporting Information, Table 6). The energy of formation of the main H-bond, E_{HB}, in $Sc(mala)_3{\cdot}H_2O$ was calculated by subtracting the E_{HB}' value from the interaction energy, e.g. E_{int}, while in $Co(mala)_3{\cdot}H_2O$ the E_{HB} value was equal to E_{int}. This led to a significant improvement in the results. The differences between the E_{HB} values in $Sc(mala)_3{\cdot}H_2O$ and $Co(mala)_3{\cdot}H_2O$ became positive, independently of the calculation variant (in particular, corrections for polarisation functions appeared negligible). In this way, the expected relationship between the calculated energies and lengths of the hydrogen bonds was achieved.

For the 1:3 hydrates, the calculations were carried out only in the simplest variant with no corrections for BSSE, ZPVE and temperature. In contrast to the expectation that three water molecules would bind to the chelate much more strongly than one, the calculated energies of gas-phase interactions of the chelates with the water trimer appeared comparable with those calculated in the same variant for the single H_2O molecule (Table 4, two last Entries). Moreover, the negative $\Delta E_{Sc/Co}$ values observed for the formation of the trihydrates, $Sc(mala)_3{\cdot}3H_2O$ and $Co(mala)_3{\cdot}3H_2O$, again led to incorrect correlation between the formation energy and the average length of the three hydrogen bonds in the trihydrates considered. This inconsistency is probably due to the significant energy required to break one hydrogen bond in the original cyclic water trimer and to stretch out the remaining two. Geometrical considerations (see above) showed that the energy must be larger in $Co(mala)_3{\cdot}3H_2O$ than in $Sc(mala)_3{\cdot}3H_2O$ because of stronger distortions of the water trimer in the former hydrate. Subtracting these contributions from the formation energies of the trihydrates would make the energies of hydrogen bonding much more negative (as expected) and restore the correct length-energy correlation. These conclusions were corroborated by the energies calculated in the SCI-PCM field.

Chelate Hydration in an Aqueous Medium. Enthalpy of Chelate Transfer

The final goal of the present work was to verify the calculated energies by comparison with the experimental data. The energies calculated for the gas phase can hardly be used for this purpose because the interaction energy significantly depends on the environment of the interacting species. The experimental values we can use for the comparison are standard enthalpies of transfer (heptane → water) of the tris(acetylacetonates) $Sc(acac)_3$ [11d] and $Co(acac)_3$ [11c] at 298 K which include the energy changes due to chelate hydration in the aqueous phase.

In order to compare these values, the enthalpy of transfer of $M(mala)_3$ chelates was calculated, taking into account solvent effects of the aqueous and heptane environments as was discussed above. The reasons why only the enthalpies and not the Gibbs free energies were used for the comparison of hydrogen bonding of water molecule(s) with the

Table 5. Enthalpies of transfer (heptane → water) of $M(mala)_3$ chelates [$kJ{\cdot}mol^{-1}$]. The energies of the species were calculated (DFT-B3LYP) in the SCI-PCM field corresponding to either water (H_2O and hydrates) or heptane (chelates); no BSSE correction

Model[a]	T, K	ΔH_{Sc}	ΔH_{Co}	$\Delta(\Delta H)_{Sc/Co}$
Field only, no hydrate formation	0 K	−36.8	−41.7	+4.9
1:1 hydrate[b]	0 K	−46.0	−50.6	+4.6
1:1 hydrate[b]	298 K	−45.1	−49.3	+4.2
1:1 hydrate, no ZPVE[b]	0 K	−54.1	−58.0	+3.9
1:3 hydrate, no ZPVE	0 K	−64.2	−67.3	+3.1
Experimental enthalpies of transfer of $Sc(acac)_3$ and $Co(acac)_3$	298 K	−41.4 ± 1.8	−52.7 ± 0.6	+11.3 ± 1.9

[a] For the energies of transfer for the formation of monohydrates, in all the calculation variants available, see Supporting information, Table 7. [b] For $Sc(mala)_3{\cdot}H_2O$, $E_{HB}' = -2.3\ kJ{\cdot}mol^{-1}$ was subtracted (see Table 4) from ΔH_{Sc}.

model and real chelates differing in the number of CH_2 groups in the ligands were as follows: (1) It was experimentally shown that for similar, coordinatively saturated beryllium β-diketonates with ligands belonging to the homologous series of acetylacetone, the enthalpies of transfer did not practically differ,[11a,28] while the free energies regularly increased with each CH_2 group added. (2) The implicit solvation model, SCI-PCM, used in the calculations does not take into account the interactions of the solute with solvent molecules which leads to formation of a solvation shell around the solute.[12] This is particularly important for aqueous solutions where the entropy term, related to this specific hydration, strongly contributes to the Gibbs energy. Therefore, to calculate the free energy of hydration of neutral molecules a special approach[29] must be used.

The electrostatic fields, used in modelling the liquid phases, modified the energies of interaction of the chelates with water to a different extent which made the energy in the cobalt system distinctly more negative than that in the scandium case, in line with the experimental observations.

Table 5 shows the enthalpies of transfer (heptane → water) of the model chelates, calculated for three different cases which refer to the species in the field of water, the species being the chelate molecule alone (no hydrate formation), the 1:1 hydrate and the 1:3 hydrate. The results shown relate to some selected variants, while the energies of transfer for the case of formation of monohydrates, calculated in all variants including BSSE corrections, the use of polarisation functions etc. are shown in Supporting Information, Table 7. The numerical values calculated with polarisation functions are somewhat less negative than the corresponding values given in Table 5, but the respective differences are very close to those in Table 5. The calculated enthalpies of transfer became more negative when more water molecules were involved in hydrogen bonding with the chelates, according to expectations. A comparison of the calculated enthalpies with the experimental standard enthalpies of transfer of the analogous tris(acetylacetonates) shows that all the values are similar, even those calculated for the case which assumed only the effect of the environment (field) with no hydrate formation. The latter result, which was rather unexpected, shows that the implicit solvation model used estimates the energy of the solute-solvent interactions in aqueous solutions very well. The calculated energy of transfer of the chelate ("solute") molecules to the field modelling water is only by about 10−20 kJ·mol^{-1} higher than the values which include the energy of hydrogen bonding of the chelate with individual (explicit) water molecule(s) which form a solvation shell around the "solute". Simply, the interactions of the "water field" with the hydrophilic sites of all "solutes" produce negative contributions to the total energies of the solutes. If these hydrophilic sites are already hydrated, the contributions are smaller. That is why the energies of chelate hydration calculated in the water field are higher than those calculated in the gas phase. (This is also in line with the observation that the E_{HB}' corrections calculated in the SCI-PCM field are distinctly smaller than those calculated in the gas phase.) Most probably, the water field interacts with the hydrated hydrophilic sites via the attached water molecule(s). The more "open" the structure of the site, the stronger the interactions. This is the case with both hydrates of Co(mala)$_3$: the lack of additional hydrogen bonding in the monohydrate and a more distorted structure of the water trimer in the trihydrate. Stronger interactions with the water field of these structures, more "open" that those in the hydrates of Sc(mala)$_3$, restore the correct relationship between the calculated energies of hydration (enthalpies of transfer) of both chelates. This consistency confirms that the model used in this work may be considered not only qualitatively but also quantitatively reliable.

In all cases, the differences between the calculated enthalpies of transfer, $\Delta(\Delta H)_{Sc/Co}$, are significantly smaller than the experimental value (Table 5) but because of simplifications in the model, they seem to be acceptable. It has been shown, therefore, that theoretical calculations can be used to evaluate the thermodynamic functions (at least the enthalpy) of the partition of neutral molecules of coordinatively saturated metal chelates between water and organic solvents. This possibility is particularly important when studying solvent extraction of metal ions.[12]

Conclusions

The calculations by means of the DFT B3LYP method on large hydrogen bonded systems, i.e. hydrates of two neutral, coordinatively saturated chelates of scandium and cobalt(III), confirm our earlier assumption that hydration of the chelates takes place in their outer coordination spheres by ligand hydration through hydrogen bonding. Simple calculations for the gas phase at 0 K result, however, in incorrect correlations between the length and the energy of the hydrogen bonds for the two hydrates. More careful examinations of the systems studied, allowed us to find interactions other than the expected hydrogen bonding which contributed to the energy of hydrate formation and disturbed the correlation. These were (1) an additional hydrogen bond in the 1:1 hydrate of the scandium (but not cobalt) chelate and (2) different distortions of the original water trimer in the 1:3 hydrates. Subtracting these contributions from the energy of hydrate formation restored the correct length vs. energy relationship for the hydrogen bonds considered.

However, the calculations of the interaction energy in the gas phase do not correctly reflect the interactions in aqueous solution because solvent effects to a different degree contribute to the total energy of the solutes (hydrates). The use of an implicit solvation model, SCI-PCM, allowed us to compare the energies calculated for this model system with the experimental standard enthalpies of transfer (heptane → water) of two analogous chelates, namely tris(acetylacetonates) of scandium and cobalt(III). In spite of simplifications in the models used and discussed in the paper, a good agreement was observed. Therefore, a correct understanding of phenomena related to the outer-sphere hydration and their quantitative description became possible.

In particular, standard enthalpies of partition of simple, coordinatively saturated metal chelates in solvent extraction systems (water/organic solvent) can be evaluated. Moreover, even the use of the most simplified solvation model, consisting of the electrostatic field alone without assuming hydrate formation, resulted in a quite satisfactory agreement with solvent extraction experiments, as far as the enthalpy of transfer was concerned.

General conclusions can also be drawn, namely (1) the present-day state of computational chemistry makes possible reliable calculations of hydrogen bonding energies in large metal-containing systems, (2) the supermolecular model well describes hydrogen bonding interactions between metal chelates and water molecules and (3) the implicit solvation model (SCI-PCM) is an adequate tool for calculating the energy of solute-solvent interactions of coordinatively saturated metal chelates and water and, in particular, standard enthalpies of transferring the chelates from an organic solvent to water.

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