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ORIGINAL RESEARCH

Bonding interactions in oxydiacetate and thiodiacetate cobalt(II) and nickel(II) complexes

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Abstract The influence of the central donor atom of the oxydiacetate and thiodiacetate ligands (oxygen and sulphur atoms, respectively) on the thermodynamic parameters for complexation reactions of the Co^{2+} and Ni^{2+} ions has been investigated using the isothermal titration calorimetry (ITC) technique and density functional theory (DFT) computations. The polarized continuum (PCM) - solvation model was employed to describe the structural factors that govern the coordination modes of the ligands (*mer* or *fac*) in the solution. The differences in the binding enthalpies of the investigated complexes were discussed based on the results obtained both from the natural bond orbital (NBO) analysis and the second-order perturbation theory.

Keywords Isothermal titration calorimetry · Oxydiacetate · Thiodiacetate · Thermodynamic parameters · Natural bond orbital analysis

Introduction

The flexible oxydiacetate (oda^{2-}) and thiodiacetate (tda^{2-}) ligands exhibit rich coordination chemistry towards metal ions. They contain five atoms that are potential donors and have great potential in constructing metal complexes with intriguing architectures and new framework topologies [1–3]. For these reasons, they are commonly used for the synthesis of coordination polymers of a potential relevance for solid state technologies [4, 5]. Furthermore, some of the oxydiacetate complexes can be used as precursors for the synthesis of metal oxides as well as mixed metal oxides that have important practical applications in several fields [6].

In the course of our ongoing studies on polycarboxylates of 3*d*-metals [7–12], we have focused our attention on oxydiacetate and thiodiacetate complexes of nickel(II) and cobalt(II). A survey of the literature reveals that in the solid state oda^{2-} when acts as a tridentate ligand adopts the *fac*-conformation in the $[Ni(oda)(H_2O)_3]1.5H_2O$ monomer [13]. Cobalt(II) oxydiacetate complexes are mainly polymeric in nature [14]. The arrangement of oda^{2-} in the cobalt(II) complexes may be planar (*mer*-disposition) or non-planar (*fac*-disposition). The complexes comprise different number of water molecules in their compositions: $[Co(oda)]_n$ (*fac*) [15], $[\{Co(oda)(H_2O)\}H_2O]_n$ (*mer*) [16], $[\{Co(oda)(H_2O)_2\}H_2O]_n$ (*mer*) [16] and $[Co(oda)(H_2O)_3]1.5H_2O$ (*fac*) [6]. It has been found that an increase of the number of the aqua ligands in the coordination sphere of Co^{2+} hinders the oxygen donor atoms of the carboxylate groups to form additional coordination of another metal [6]. The tda^{2-} ligand exists invariably in the *fac*-coordinating conformation forming the monomeric $[Ni(tda)(H_2O)_3]$ complex [17], as well as polymeric $[Co(tda)(H_2O)]_n$ and monomeric $[Co(tda)(H_2O)_3]$ complexes [14]. In aqueous solutions, oxydiacetate and thiodiacetate complexes of Co^{2+} and Ni^{2+} exist as monomer species [14]. This is confirmed by the fact that two coordination water molecules can easily be displaced from these species upon the reaction with bidentate N-donor ligands [18, 19].

The solution chemistry of oxydiacetate and thiodiacetate cobalt(II) and nickel(II) complexes is comparatively less developed than that of the solid state chemistry. In particular, there are no reports on the influence of the central donor atoms of oda^{2-} and tda^{2-} (oxygen and sulphur atoms, respectively) on thermodynamic parameters for complexation reactions of the Co^{2+} and

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Ni^{2+} ions. Thus, it was, among others, the reason that prompted us to embark on these studies. The dependence of thermodynamic properties on structural details is essential to comprehend how the investigated interactions occur in solutions. In this paper, we discuss and elucidate the details of the donor-acceptor interactions based on the isothermal titration calorimetry data and density functional theory (DFT) computations.

Experimental

Materials

All reagents, namely $Co(NO_3)_2 \cdot 6H_2O$ (≥99%), $Ni(NO_3)_2 \cdot 6H_2O$ (≥99.999%), 2,2′-oxydiacetic acid (H_2oda) (≥98%), 2,2′-thiodiacetic acid (≥98%) (H_2tda) and 2-(N-morpholino)ethanesulfonic acid hydrate (≥99%) (Mes) were purchased from Sigma - Aldrich Chemical Corp. and used as received.

Methods

Isothermal titration calorimetry

All ITC experiments were performed at 298.15 K using the AutoITC isothermal titration calorimeter (MicroCal Inc. GE Healthcare, Northampton, USA). The details of the measuring devices and experimental setup were described previously [20]. All reagents were dissolved directly into the 100 mM buffer solution of Mes. The pH of the buffer solution was adjusted to 6.0 with 0.1 M NaOH. The ionic strength was maintained by the components of the buffers. The experiment consisted of injecting of 10.02 μL (29 injections, 2 μL for the first injection only) of ca 30 mM of the buffered solution of H_2oda or H_2tda into the reaction cell which initially contained ca of 1–2 mM of the buffered solution of the suitable salt (Co^{2+}, Ni^{2+}). For each experimental condition, a blank was performed by injecting the titrant solution into the cell filled with the buffer only. This blank was subtracted from the corresponding titration to account for the heat of dilution. All solutions were degassed prior to the titration. The titrant was injected at 5-min intervals to ensure that the titration peak returned to the baseline before the next injection. Each injection lasted 20 s. For homogeneous mixing in the cell, the stirrer speed was kept constant at 300 rpm. The data, specifically the heat normalized per mole of injectant, were processed with Origin 7 from MicroCal.

Potentiometric titrations

Potentiometric titrations (PT) were performed in a 30-mL thermostated (298.15 ± 0.10 K) cell using the Cerko Lab System microtitration unit fitted with the 5-mL Hamilton's syringe (the syringe calibration constant $k = 4.15$), the pH combined electrode (Schott – BlueLine 16 pH type) and a self-made measuring cell equipped with a magnetic stirrer. The temperature was controlled using the Lauda E100 circulation thermostat. The electrode was calibrated according to IUPAC recommendations [21] and already checked procedures [22, 23]. The composition of the titrand solution used in the experiments was as follows: 1 mM Co^{2+} or Ni^{2+}, 1.5 mM H_2oda or 1.5 mM H_2tda and 4 mM HNO_3. The solutions (V_o = 5.0 mL) were potentiometrically titrated with the standardized 50 mM NaOH solution in the pH range from 2.5 to 11.0. The titrant was added to the titrand in increments of 0.02 mL, with a pause of 120 s. Each titration was repeated at least three times in order to check the reproducibility of the data. The equilibrium constants defined by Eqs. (1) and (2):

$$pM + qL + rH = M_pL_qH_r \quad (1)$$

$$\beta_{pqr} = \frac{[M_pL_qH_r]}{[M]^p[L]^q[H]^r} \quad (2)$$

(where M is Co^{2+} or Ni^{2+}, L denotes the oda^{2-} or tda^{2-} ion, H is the proton and p, q, r are stoichiometric coefficients for the reaction) were refined by least-squares calculations using the Hyperquad2008 (ver. 5.2.19) computer program [24]. The pK_a values of the acids (H_2oda or H_2tda) and the binding constants of the investigated complexes were obtained by adapting the equilibrium model to the potentiometric titration (PT) data (Table 1). The following model has provided the best fitting of the calculated data to the experimental ones (the charges of ions are omitted for the sake of clarity):

$$L + H = LH \quad \beta_{011} = K_{a1} = \frac{[LH]}{[L][H]}$$

$$L + 2H = LH_2 \quad \beta_{012} = K_{a1}K_{a2} = \frac{[LH_2]}{[L][H^2]}$$

$$M + L = ML \quad \beta_{110} = K = \frac{[ML]}{[M][L]}$$

$$M + L + 2OH = ML(OH)_2 \quad \beta_{11-2} = \frac{[ML(OH)]}{[M][L][H]^{-2}}$$

The formation of the hydroxo complexes were taken into account in the calculation of the stability constants. The $\log\beta_{01-2}$ are −14.12 (±0.07), −14.68 (±0.09), −14.94 (±0.11) and −14.35 (±0.03) for $Ni(oda)(OH)_2^{2-}$, $Ni(tda)(OH)_2^{2-}$, $Co(oda)(OH)_2^{2-}$ and $Co(tda)(OH)_2^{2-}$, respectively.

Computations: ab initio calculations

The equilibrium geometries and harmonic vibrational frequencies of the complexes were calculated using the density

Table 1 Thermodynamic parameters of Co^{2+} and Ni^{2+} binding to the ligand (oda^{2-} or tda^{2-}) at 298.15 K

Potentiometric titration		Isothermal titration calorimetry	
$Co(oda)(H_2O)_3$	$Co(tda)(H_2O)_3$	$Co(oda)(H_2O)_3$	$Co(tda)(H_2O)_3$
pK_{a1} = 3.01 (±0.06)	pK_{a1} = 3.20 (±0.02)	$\log K_{ITC}$ = 3.21 (±0.02)	$\log K_{ITC}$ = 3.52 (±0,01)
pK_{a2} = 4.08 (±0.05)	pK_{a2} = 4.22 (±0.03)	ΔH_{ITC} [kcal/mol] = 3.81 (±0.06)	ΔH_{ITC} [kcal/mol] = 2.42 (±0.02)
$\log K_{CoODA}$ = 3.41 (±0.07)	$\log K_{CoTDA}$ = 3.65 (±0.08)	$\log K$ = 3.38 (±0.03)	$\log K$ = 3.70 (±0.01)
		ΔG [kcal/mol] = −4.61 (±0.04)	ΔG [kcal/mol] = −5.05 (±0.01)
		ΔH [kcal/mol] = 3.96 (±0.06)	ΔH [kcal/mol] = 2.59 (±0.02)
		$T\Delta S$[kcal/mol] = 8.57 (±0.07)	$T\Delta S$[kcal/mol] = 7.64 (±0.02)
$Ni(oda)(H_2O)_3$	$Ni(tda)(H_2O)_3$	$Ni(oda)(H_2O)_3$	$Ni(tda)(H_2O)_3$
pK_{a1} = 2.75 (±0.04)	pK_{a1} = 3.19 (±0.04)	$\log K_{ITC}$ = 3.31 (±0.01)	$\log K_{ITC}$ = 3.97 (±0.02)
pK_{a2} = 4.12 (±0.04)	pK_{a2} = 3.94 (±0.05)	ΔH_{ITC} [kcal/mol] = 3.72 (±0.04)	ΔH_{ITC} [kcal/mol] = 1.56 (±0.01)
$\log K_{NiODA}$ = 3.46 (±0.09)	$\log K_{NiTDA}$ = 4.02 (±0.07)	$\log K$ = 3.49 (±0.01)	$\log K$ = 4.15 (±0.02)
		ΔG [kcal/mol] = −4.76 (±0.01)	ΔG [kcal/mol] = −5.66(±0.03)
		ΔH [kcal/mol] = 3.91 (±0.04)	ΔH [kcal/mol] = 1.73 (±0.01)
		$T\Delta S$[kcal/mol] = 8.57 (±0.04)	$T\Delta S$[kcal/mol] = 7.39 (±0.03)

functional theory (DFT) method with the B3LYP [25, 26] functional and the 6-31++G(d,p) basis set [27, 28]. To describe the effect of the solvent (water) on the geometry structures and energy of the molecules, the polarized continuum (PCM) [29–31] solvation model was employed. The partial atomic charges and the relevant orbital populations were computed by the natural bond orbital (NBO) analysis scheme [32–36]. All calculations were performed with the Gaussian 09 program package [37].

Results and discussion

The binding constants (K_{ITC}) and binding enthalpies (ΔH_{ITC}) of the interactions of oda^{2-} and tda^{2-} with Co^{2+} and Ni^{2+} were obtained directly from ITC experiments (Table 1). To eliminate a pH mismatch between a titrant (a syringe solution) and a titrand (a sample cell solution) maintaining a constant pH of a solution is required. Otherwise, the heat effects that are not connected with the metal – ligand interactions are generated on account of the neutralization reaction, $H_3O^+ + OH^- = 2H_2O$ [38]. For this reason, the ITC experiments were carried out in the Mes buffer that is commonly used in calorimetric studies [9, 10, 39]. In such a case, the K_{ITC} and ΔH_{ITC} parameters (marked by the subscript ITC) are so called condition-dependent parameters as their values depend on the pH of a buffer solution as well as the metal (Co^{2+} and Ni^{2+}) – buffer (Mes) interactions. Representative binding isotherms for Ni-H_2oda and Ni-H_2tda interactions are shown in Fig. 1.

K_{ITC} is conditioned by the Mes competition with the ligand, L, (L denotes oda^{2-} and tda^{2-}) for the metal, M, (M denotes Co^{2+} or Ni^{2+}) as well as the proton competition with the metal for the buffer and ligand (Eq. 3):

$$K_{ITC} = \frac{K}{\left(1 + \frac{[H^+]}{K_{a_2}} + \frac{[H^+]^2}{K_{a_2} \cdot K_{a_1}}\right) \cdot \frac{K_{M(Mes)} \cdot [Mes]}{1 + [H^+] / K_{MesH}}} \quad (3)$$

where K is the pH- and buffer-independent metal-ligand binding constant, K_a is the acid dissociation constant of the ligand (K_{a1}: $H_2L = HL^- + H^+$, K_{a2}: $HL^- = L^{2-} + H^+$), $K_{M(Mes)}$ is the metal-buffer binding constant and K_{MesH} is the MesH acid dissociation constant ($MesH^{\pm} = Mes^- + H^+$). The $K_{M(Mes)}$ [8] and $_KMesH$ [40] values were taken from the literature. For calculations of K (Eq. 1) the pK_{a1} and pK_{a2} values obtained in our laboratory were used (Table 1). The $\log K$ values calculated based on Eq. 1 are in good agreement, in the range of experimental error, with those obtained from potentiometric measurements (Table 1).

ΔH_{ITC} is the sum of all energetic effects generated during ITC measurements. To calculate the condition-independent enthalpy of the complex formation (ΔH), the heat effects which are not connected with the metal-ligand interactions were taken into account. They are as follows: the enthalpy

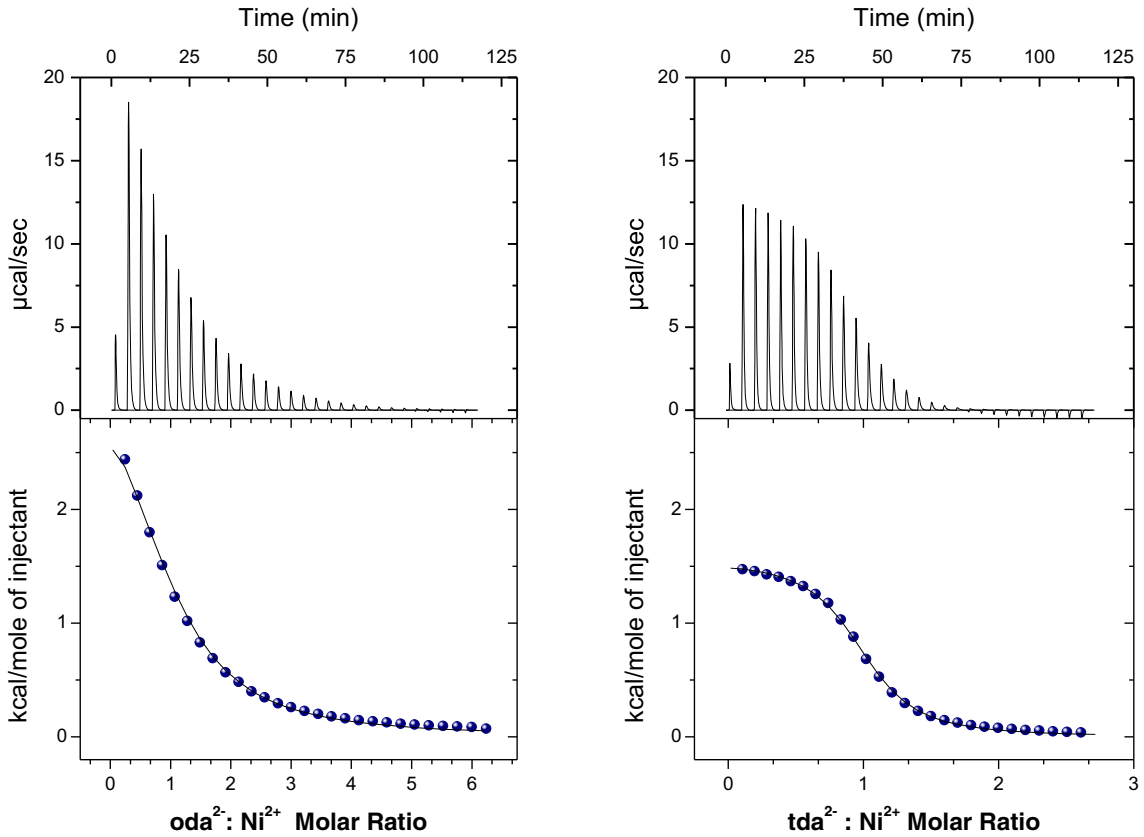

Fig. 1 Calorimetric titration isotherms of the binding interactions between oda^{2-} and Ni^{2+} (*left*) and tda^{2-} and Ni^{2+} (*right*) in the 100 mM Mes buffer of the pH of 6.0, at 298.15 K

of the proton dissociation from the ligand (ΔH_{H2L}, ΔH_{HL}) [41], the enthalpy of the buffer ionization (ΔH_{BH}) [40] as well as the enthalpy formation and the stability constant of the metal-buffer complex (ΔH_{MB} and $K_{M(Mes)}$, respectively) [8].

The change in the enthalpy of the cobalt(II) and nickel(II) complexation, ΔH_{ML}, by oda^{2-} and tda^{2-} was calculated using the equation based on Hess's law (Eq. 4) (Table 1) [42].

$$\Delta H_{ITC} = -\alpha_{MB}\Delta H_{MB} - \alpha_{HL}\Delta H_{HL} - \alpha_{H2L}\Delta H_{H2L} + (\alpha_{HL} + 2\alpha_{H2L})\Delta H_{BH} + \boldsymbol{\Delta H_{ML}} \quad (4)$$

Where α are the coefficients that indicate the percentage of the particular chemical species in the solution under experimental conditions (α_{MB} – the metal-buffer complex, α_{HL} - the $Hoda^-$ or $Htda^-$ ion and α_{H2L} – the H_2oda or H_2tda acid). At pH 6 $\alpha_{H2L} << \alpha_{HL}$ and thus the Eq. 2 can be simplified (Eq. 5):

$$\Delta H_{ITC} = -\alpha_{MB}\Delta H_{MB} - \alpha_{HL}\Delta H_{HL} + \alpha_{HL}\,\Delta H_{BH} + \boldsymbol{\Delta H_{ML}} \quad (5)$$

Then, the free energy of the binding (ΔG) and entropy change (ΔS) were calculated using the standard thermodynamic relationships: $\Delta G = -RT\ln K = \Delta H - T\Delta S$ (Table 1).

The binding constants of the cobalt(II) and nickel(II) oxydiacetate complexes are slightly lower than those of the corresponding thiodiacetate ones ($\log K_{Co(oda)} < \log K_{Co(tda)}$ and $\log K_{Co(oda)} < \log K_{Ni(tda)}$). This is in line with the general rule according to which the greater basicity of the ligand the more stable complexes are formed [43]. The binding constant (K), and thus the change in the free energy (ΔG) provide only general information about the thermodynamic stability of the complexes. It encompasses all the effects accompanying ligand binding to a metal ion. The knowledge of thermodynamic parameters (ΔH, ΔS) of a reaction enables a better understanding of the nature of chemical processes and factors affecting the stability of the resulting complexes than does that of simple binding constant, K.

Thermodynamic parameters (Table 1) revealed that the formation of the complexes is an entropy-driven process ($|\Delta H| < |T\Delta S|$). The positive binding enthalpy reflects the stronger interactions of the metal ions with the water (as a solvent) related to those with the ligands. It manifests itself in consuming more heat on a dehydration reaction of the metal ions, $[M(H_2O)_6]^{2+}$, (an endothermic effect) than it is released on account of the metal-ligand bond formation (an exothermic effect).

Despite the fact that both oda^{2-} or tda^{2-} ligands form two five-member chelate rings the binding enthalpy of thiodiacetate complexes is lower than that of the

corresponding oxydiacetate complexes (Table 1). Taking into account the same composition of the coordination sphere of the central ion, comprising one tridentate chelating ligand (oda^{2-} or tda^{2-}) and three aqua ligands, the difference in the binding enthalpies of the investigated complexes stems from the different central donor atoms of the oda^{2-} and tda^{2-} ligands (oxygen and sulphur atoms, respectively). Thus, it can be supposed that the more covalent character of the M^{2+}-$S_{(thioether)}$·bond (thiodiacetate complexes) in comparison to the M^{2+}-$O_{(ethereal)}$·bond (oxydiacetate complexes) is responsible for the release of a larger amount of the energy during the formation of the M^{2+}-thiodiacetate complexes. This assumption has subsequently been verified by DFT calculations.

To get some inside into geometry structures of the investigated complexes in the solution and the relative stabilities of the *mer* and *fac* conformation of oda^{2-} and tda^{2-} ligands in the coordination sphere of the Co^{2+} and Ni^{2+} ions, ab initio calculations involving the polarized continuum (PCM) - solvation model were performed. A computed energy difference (ΔE) between *fac* and *mer* isomers of oda^{2-} is close to zero for the nickel(II) complex and ca. 0.5 kcal/mol for the cobalt(II) complex. It is therefore possible to presume that both isomers can co-exist in the solution. The largest differences in ΔE have been found for thiodiacetate complexes. The *fac* arrangement of the tda^{2-} ligand in the nickel(II) complex is lower in the energy by ca. 7 kcal/mol than the *mer*-disposition whereas for the cobalt(II) complex only the *fac* conformation of tda^{2-} is geometrically stable. The optimized geometries of the complexes together with the selected structural parameters are depicted in Fig. 2.

The calculated M-$O_{(ethereal)}$·and M-$S_{(thioether)}$ distances in the investigated complexes are well reproduced with the experimental ones (Table 2). A significant variation in M-$O_{(ethereal)}$ bond distances occurs in going from the *mer*-conformation to the *fac*-conformation (0.08 and 0.06 Å for $Ni(oda)(H_2O)_3$ and $Co(oda)(H_2O)_3$, respectively). Furthermore, the computed M-$O_{carbox.}$ bonds appear somewhat overestimated. The differences are higher for cobalt complexes which exist in the solid state in the polymeric form. Taking into account the fact that the oxygen atoms of the carboxylate groups interact with another cobalt(II) ion in the solid state the calculated differences that do not exceed 0.07 Å are satisfactory. It is also worth mentioning that the presence of a central oxygen or sulphur atom in oda^{2-} and tda^{2-}, respectively, affects the conformation on the ligand. The longer M-$S_{(thioether)}$ distance in comparison to the M-$O_{(ethereal)}$ distance favours non-planar arrangement (*fac*) of the ligand (Fig. 3). The two five-membered rings forming by tda^{2-} are not so rigid as it would be if the ligand adopts the *mer* disposition. This finding explains the computed energy difference (ΔE) between *fac* and *mer* isomers in nickel(II) thiodiacetate complexes as well as the stability of the *fac* conformer of $Co(tda)(H_2O)_3$ only. The geometric parameters of cobalt(II) thiodiacetate complexes could not be compared with the

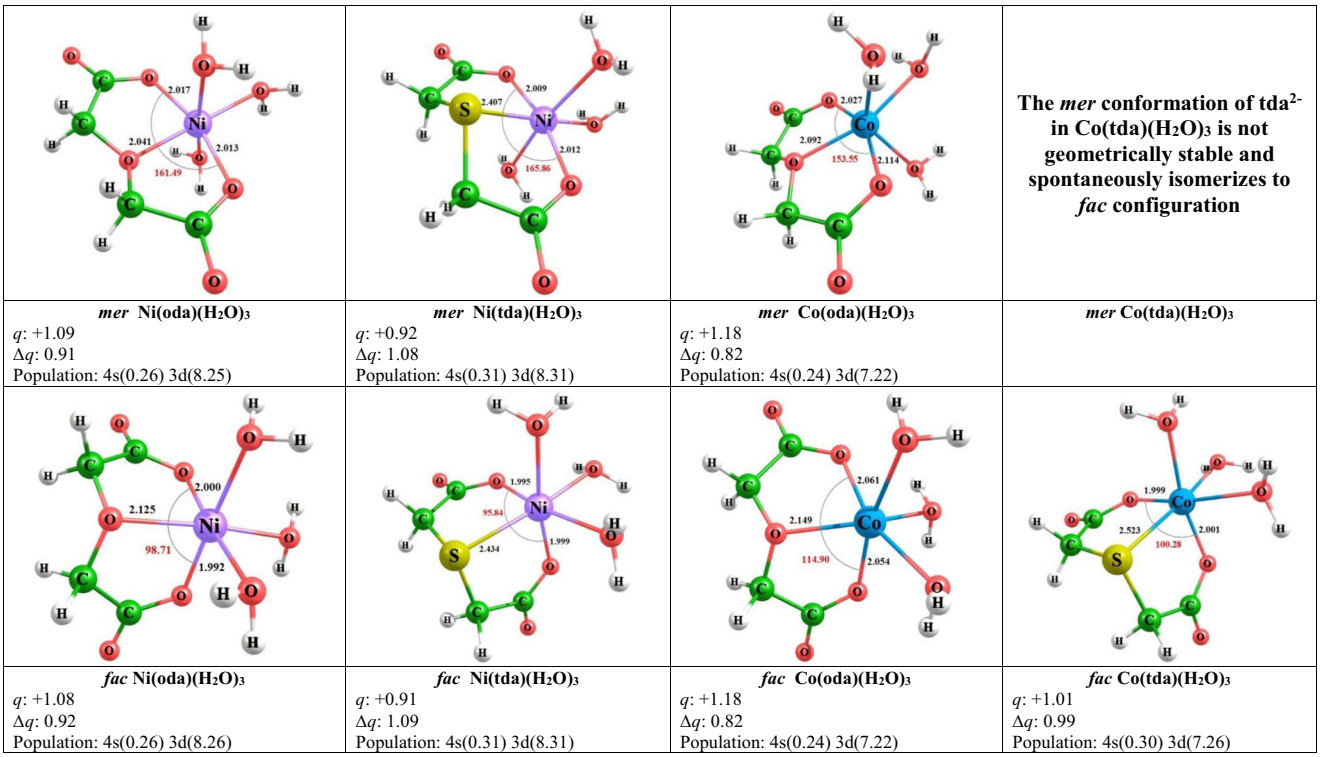

Fig. 2 Selected structural parameters (bond distances in Å and angles in °) of the optimized geometries and computed bonding characteristics: q – the natural atomic charges, Δq – the transferred charge to the metal cations and the relevant orbital populations given in electrons (population)

Table 2 Selected experimental geometrical parameters of the investigated complexes

Compound	M-X [Å][a]	M-$O_{carbox.}$ [Å]	$O_{carbox.}$-M-$O_{carbox.}$ [°]	References
fac Ni(oda)$(H_2O)_3$	2.130	2.040 2.010	91.80	[13]
fac Ni(tda)$(H_2O)_3$	2.415	2.034 2.054	89.22	[17]
fac Co(oda)	2.132	2.073 2.184	101.90	[15]
mer [{Co(oda)(H_2O)}$H_2O]_n$	2.108	2.085 2.100	152.7	[16]
mer [{Co(oda)$(H_2O)_2$}$H_2O]_n$	2.073	2.100 2.106	149.9	[16]

[a] M = Co or Ni; X = $O_{ethereal}$ or $S_{thioether}$

experimental ones as the structures of solid [Co(tda)$(H_2O)_n$] and [Co(tda)$(H_2O)_3$] were determined only by the IR inspection [14].

The differences in the binding enthalpy of the resulting complexes result mainly from the properties of the centrals donor atoms of the oda^{2-} and tda^{2-} ligands. The NBO analysis has revealed that the tda^{2-} ligands exert somewhat larger the ligand-to-metal donation (the charge transfer) than the oda^{2-} ones, although the M^{2+}-$O_{(ethereal)}$ bond distance is shorter in comparison to the M^{2+}-$S_{(thioether)}$·distance (Fig. 2). The donations go in similar magnitude to the valence s and p orbitals. For the same metal ion, the conformation of the ligand (*mer* or *fac*) does not affect the magnitude of the donation. The results obtained from the NBO approach correlate well with the experimental values of the binding enthalpies. It can be concluded that the stronger ligand donation the larger covalent contribution in the bonding. Consequently, the binding enthalpies are lower due to the release of a larger amount of the heat during the formation of the more covalent M^{2+}-$S_{(thioether)}$ bonds in the thiodiacetate complexes than it is in the case of the M^{2+}-$O_{(ethereal)}$ bond formation in oxydiacetate complexes.

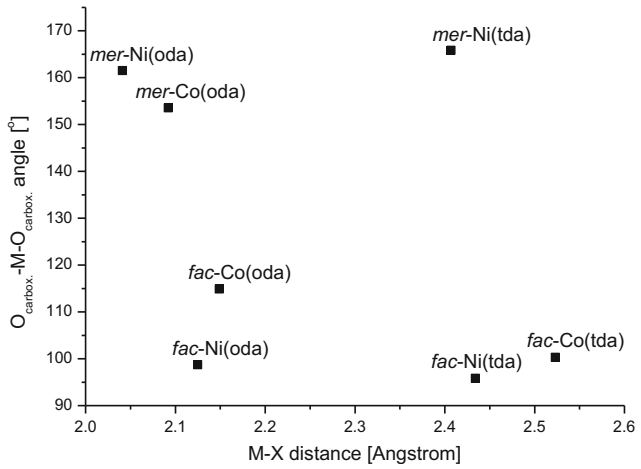

Fig. 3 The plot of the M-X distance [Å] (M = Co or Ni; X = $O_{ethereal}$ or $S_{thioether}$) vs. the $O_{carbox.}$-M-$O_{carbox.}$ angle [°] showing interdependence between the M-X bond distance and the conformation of the oda^{2-} and tda^{2-} ligands

Furthermore, in order to estimate the importance of the electron delocalization between the oda^{2-} and tda^{2-} ligands with Co^{2+} or Ni^{2+}, we calculated the second-order perturbation energy *E(2)* of the occupied NBO(i) of an electron donor which interacts with the unoccupied NBO(j) of an electron acceptor. According to the analysis, the stabilization energy *E(2)* is given by the expression:

$$E(2) = \Delta E_{ij} = q_i \frac{F^2_{(ij)}}{\varepsilon_j - \varepsilon_i} \quad (6)$$

where q_i is the donor orbital occupancy, ε_i, ε_j are diagonal elements (orbital energies) and *F(i,j)* is the off-diagonal NBO Fock matrix element.

Our calculations have revealed that the most stabilizing interactions between the oda^{2-} or tda^{2-} ligands and Ni^{2+} involve the lone pairs of oxygens (in Ni(oda)$(H_2O)_3$) or oxygens and sulphur (in Ni(tda)$(H_2O)_3$) with antibonding NBOs of Ni^{2+}. In particular, the following values of *E(2)* were obtained: 140.78, 188.93, 169.27, and 190.04 kcal/mol for *mer*-Ni(oda)$(H_2O)_3$, *fac*-Ni(oda)$(H_2O)_3$, *mer*-Ni(tda)$(H_2O)_3$ and *fac*-Ni(tda)$(H_2O)_3$, respectively. Interestingly, the listed donations in *mer*-Ni(oda)$(H_2O)_3$/*fac*-Ni(oda)$(H_2O)_3$ and *mer*-Ni(tda)$(H_2O)_3$/*fac*-Ni(tda)$(H_2O)_3$ isomeric structures are always larger in *fac* configurations, whereas in the complexes adopting the same configuration but containing different ligands (i.e., *mer*-Ni(oda)$(H_2O)_3$/*mer*-Ni(tda)$(H_2O)_3$ and *fac*-Ni(oda)$(H_2O)_3$/*fac*-Ni(tda)$(H_2O)_3$) larger *E(2)* values are predicted for NiTDA systems. In addition, our analysis also indicates that much weaker interactions occur between the occupied σC-O (in Ni(oda)$(H_2O)_3$ complexes) and σC-O and σC-S bonds (in Ni(tda)$(H_2O)_3$) antibonding NBOs of Ni^{2+} and the values of *E(2)* are equal to: 25.20, 34.77, 40.86, and 28.22 kcal/mol for *mer*-Ni(oda)$(H_2O)_3$, *fac*-Ni(oda)$(H_2O)_3$, *mer*-Ni(tda)$(H_2O)_3$ and *fac*-Ni(oda)$(H_2O)_3$, respectively.

As far as the Co(oda)$(H_2O)_3$ and Co(tda)$(H_2O)_3$ complexes are concerned, the similar tendencies are observed, namely, the donations to the Co atom occur mainly from the lone pairs of oxygens (*E(2)* of 158.74 kcal/mol for *mer*-Co(oda)$(H_2O)_3$ and 164.40 kcal/mol for *fac*-Co(oda)$(H_2O)_3$) and oxygens and sulphur (E(2) = 174.19 kcal/mol for *fac*-Co(tda)$(H_2O)_3$), while minor donations occur from σC-O in *mer*-Co(oda)$(H_2O)_3$ and *fac*-Co(oda)$(H_2O)_3$, (29.07 kcal/mol and 28.18 kcal/mol, respectively) and σC-O and σC-S bonds in *fac*-Co(tda)$(H_2O)_3$ (25.23 kcal/mol). Similarly to the nickel complexes, the larger stabilization energy involving lone pairs of oxygens with the antibonding NBOs of Co in *mer*-Co(oda)$(H_2O)_3$ and *fac*-Co(oda)$(H_2O)_3$ is observed in the *fac* isomer whereas in *fac*-Co(oda)$(H_2O)_3$ and *fac*-Co(tda)$(H_2O)_3$ complexes such donations (from oxygens in

the case of oda^{2-} or oxygens and sulphur in the case of tda^{2-}) is larger in the $Co(tda)(H_2O)_3$ complex.

Conclusions

The isothermal titration calorimetry (ITC) technique supported by ab initio calculations (DFT) involving the polarized continuum (PCM) - solvation model have successfully been applied for studying complexation reactions of Co^{2+} and Ni^{2+} ions with oxydiacetate (oda^{2-}) and thiodiacetate (tda^{2-}) ligands. The quantification of the metal (Co^{2+} and Ni^{2+}) – buffer (Mes) interactions and incorporation them into the ITC data analysis enabled to obtain the pH-independent and buffer-independent thermodynamic parameters (K, ΔG, ΔH and ΔS) for the reactions under study.

It has been found that the stability of thiodiacetate complexes is slightly higher than those of the corresponding oxydiacetate complexes: ($\log K_{Co(oda)} < \log K_{Co(tda)}$ and $\log K_{Co(oda)} < \log K_{Ni(tda)}$). The formation of the complexes is an entropy-driven process ($|\Delta H| < |T\Delta S|$). However, the binding enthalpy is lower for thiodiacetate complexes.

The M-X bond distance (X denotes the central donor atom: $O_{ethereal}$ or $S_{thioether}$) governs the conformation of the ligand in the coordination sphere of the metal ion. The elongation of the M-X distance favours the *fac*-disposition because of the lesser strain of the bond angles in two five membered rings formed by the ligand.

The major structural factor for the amount of ligand-to-metal charge transfer (Δq) is central donor atom of the oda^{2-} and tda^{2-} ligands (oxygen and sulphur atoms, respectively). The metals with tda^{2-} receive the largest amount of charge from the ligand. The conformation of the ligand (*mer* or *fac*) does not affect the magnitude of the donation. The donations go in the similar magnitude to the valence s and p orbitals. This phenomenon correlates well with the second-order perturbation energies, *E(2)* obtained from the NBO approach. Thus, it can be concluded that the binding enthalpies of the investigated complexes depend on the ionic vs. covalent contribution in the M^{2+}-$S_{(thioether)}$ and M^{2+}-$O_{(ethereal)}$ bonds. The lower ΔH the more covalent contribution in the bonding is observed. Accordingly, it could be postulated that the binding enthalpy can serve as a useful thermodynamic parameter for the assessment of the donor-acceptor interactions.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

References

1. Qiu JZ, Wang LF, Chen YC, Zhang ZM, Li QW, Tong ML (2016) Chem Eur J 22:802–808
2. Khullar S, Mandal SK (2014) Cryst Growth Des 14:6433–6444
3. Zhou Q, Yang F, Liu D, Peng Y, Li G, Shi Z, Feng S (2012) Inorg Chem 51:7529–7536
4. Lu G, Lieberwirth I, Wegner G (2006) J Am Chem Soc 128:15445–15450
5. Baggio R, Garland MT, Moreno Y, Peña O, Perec M, Spodine E (2000) Dalton Trans 13:2061–2066
6. Grirrane A, Pastor A, Álvarez E, González M, Galindo A (2007) Polyhedron 26:3343–3349
7. Wyrzykowski D, Tesmar A, Jacewicz D, Pranczk J, Chmurzyński L (2014) J Mol Recogn 27:722–726
8. Wyrzykowski D, Pilarski B, Jacewicz D, Chmurzyński L (2013) J Therm Anal Calorim 111:1829–1836
9. Wyrzykowski D, Zarzeczańska D, Jacewicz D, Chmurzyński L (2011) J Therm Anal Calorim 105:1043–1047
10. Wyrzykowski D, Chmurzyński L (2010) J Therm Anal Calorim 102:61–64
11. Wyrzykowski D, Czupryniak J, Ossowski T, Chmurzyński L (2010) J Therm Anal Calorim 102:149–154
12. Wyrzykowski D, Inkielewicz-Stępniak I, Czupryniak J, Jacewicz D, Ossowski T, Woźniak M, Chmurzyński L (2013) Z Anorg Allg Chem 639:1795–1799
13. Baggio R, Garland MT (2000) M Perec. Inorg Chim Acta 310:103–109
14. Grirrane A, Pastor A, Álvarez E, Mealli C, Ienco A, Rosa P, Galindo A (2007) Eur J Inorg Chem 22:3543–3552
15. Forster PM, Cheetham AK (2004) Micropor Mesopor Mater 73:57–64
16. Jiang C, Wang ZY (2003) Polyhedron 22:2953–2959
17. Alarcón-Payer C, Pivetta T, Choquesillo-Lazarte D, González-Pérez JM, Crisponi G, Castiñeiras A, Niclós-Gutiérrez J (2004) Inorg Chem Commun 7:1277–1280
18. Wyrzykowski D, Pranczk J, Jacewicz D, Tesmar A, Pilarski B, Chmurzyński L (2014) Open Chem 12:107–114
19. Wyrzykowski D, Pranczk J, Jacewicz D, Tesmar A, Pilarski B, Chmurzyński L (2014) Open Chem 13:2391–5420
20. Tesmar A, Wyrzykowski D, Jacewicz D, Żamojć K, Pranczk J (2016) L Chmurzyński. J Therm Anal Calorim 126:97–102
21. Brandariz I, Barriada J, Vilarino T, de Vicente MS (2004) Monatsh Chem 135:1475–1488
22. Chmurzyński L (1996) Anal Chim Acta 329:267–274
23. Chmurzyński L, Nesterowicz M, Wawrzyniak G, Kaczmarczyk E, Warnke Z (1996) Aust J Chem 49:931–942
24. Gans P, Sabatini A, Vacca A (1996) Talanta 43:1739–1753
25. Lee C, Yang W, Parr RG (1988) Phys Rev B 37:785–789
26. Becke AD (1988) Phys Rev A 38:3098–3100
27. McLean AD, Chandler GS (1980) J Chem Phys 72:5639–5648
28. Krishnan R, Binkley JS, Seeger R, Pople JA (1980) J Chem Phys 72:650–654
29. Miertus S, Scrocco E, Tomasi J (1992) Chem Phys 55:117–129
30. Miertus S, Tomasi J (1982) Chem Phys 65:239–245

31. Cossi M, Barone V, Cammi R, Tomasi J (1996) Chem Phys Lett 255:327–335
32. Foster JP, Weinhold F (1980) J Am Chem Soc 102:7211–7218
33. Reed AE, Weinhold F (1983) J Chem Phys 78:4066–4073
34. Reed AE, Weinstock RB, Weinhold F (1985) J Chem Phys 83:735–746
35. Carpenter JE, Weinhold F (1988) J Mol Struct 46:41–62
36. Reed AE, Curtiss LA, Weinhold F (1988) Chem Rev 88:899–926
37. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Scalmani G, Barone V, Mennucci B, Petersson GA, Nakatsuji H, Caricato M, Li X, Hratchian HP, Izmaylov AF, Bloino J, Zheng G, Sonnenberg JL, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Vreven T, Montgomery JA, Peralta JE, Ogliaro F, Bearpark M, Heyd JJ, Brothers E, Kudin KN, Staroverov VN, Kobayashi R, Normand J, Raghavachari K, Rendell A, Burant JC, Iyengar SS, Tomasi J, Cossi M, Rega N, Millam NJ, Klene M, Knox JE, Cross JB, Bakken V, Adamo C, Jaramillo J, Gomperts R, Stratmann RE, Yazyev O, Austin AJ, Cammi R, Pomelli C, Ochterski JW, Martin RL, Morokuma K, Zakrzewski VG, Voth GA, Salvador P, Dannenberg JJ, Dapprich S, Daniels AD, Farkas Ö, Foresman JB, Ortiz JV, Cioslowski J, Fox DJ (2009) Gaussian 09, Revision B01. Wallingford CT, Gaussian, Inc
38. Harty M, Bearne SL (2016) J Therm Anal Calorim 123:2573–2582
39. Christensen T, Gooden DM, Kung JE, Toone EJ (2003) J Am Chem Soc 125:7357–7366
40. Goldberg RN, Kishore N, Lennen RM (2002) J Phys Chem Ref Data 31:231–270
41. Wyrzykowski D, Anusiewicz I, Pilarski B, Jacewicz D, Chmurzyński L (2013) Inorg Chim Acta 405:163–168
42. Grossoehme NE, Spuches AM, Wilcox DE (2010) J Biol Inorg Chem 15:1183–1191
43. Barszcz B (2005) Coord Chem Rev 249:2259–2276