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Estimation of coordination bond energies of NH_3, H_2O and Et_2NH ligands in the Ni(II) and Cu(II) complexes

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Abstract Tridentate ligands 2-hydroxyphenylsalicylaldimine ($SAPH_2$), 2-hydroxyphenyl-2-hydroxy-1-naphtaldimine ($NAPH_2$) and Ni(II) complexes with multidentate ligand Bis-N·N′-(salicylidene)-1,3-propanediamine (LH_2) as well as mononuclear complex of Cu(II) were prepared using the same multidentate ligand. Diethylamine (Et_2NH), NH_3 and H_2O monodentate ligands were bound to these complexes coordinatively. The heat absorbed at the temperatures where these ligands thermally dissociated from the complexes were measured using the TG and DSC methods. It is assumed that the states both of the complexes with and without the monodentate ligands are solid and coordination bond energy for the monodentate ligand is calculated. It is seen that these calculated coordination bond energies are comparable with hydrogen bond energies.

Keywords Bond energy · Coordination bonds · DSC · Schiff bases · Thermal analysis

Introduction

It is known since 1965 that tridentate ligands of the type ONO and ONS form binuclear complexes with first series of transition elements. All the complexes that they form with $Ni^{2+}$and Cu^{2+} ions are particularly well known [1–5].

It has been reported by many researchers that these binuclear complexes transform into mononuclear complexes in the presence of a monodentate nitrogen ligand such as NH_3, Py [4–11].

It has been reported that formation of a mononuclear complex, by taking up a monodentate ligand and later removal of this monodentate ligand thermally to finally end up with a binuclear complex again, is a reversible process [6]. Both states are solid and the coordination sphere where the metal ions are located have the same geometrical structure; square plane. In this case, if it is accepted that the crystal energies of both bi- and mononuclear states [(I) and (II) states] are about the same, it is possible to experimentally obtain the coordination bond energy binding the monodentate ligand to the metal. To this aim it is sufficient to measure the heat absorbed at the temperature that the monodentate ligand leaves the structure. If the monodentate ligand leaves the structure between T_1 and T_2, the peak temperature of the DTA peak can be accepted as the temperature where the monodentate ligand leaves the structure (T_{DTA}). If the heat absorbed between T_1 and T_2 is Q, then Q is thermodynamically equal to the sum given below.

$$Q = Q_{vap} + Q_1 + Q_2 + \Delta Q_{crystal} + \Delta H_b \qquad (I)$$

Q_{vap}	Evaporation energy of the monodentate ligand taken from published literature
Q_1	The heat taken up by the monodentate ligand in liquid state starting from the initial temperature of the study until the boiling temperature

$$Q_1 = C * \Delta T \qquad (II)$$

C	Liquid state molar specific heat
ΔT	Temperature difference between the initial temperature and the boiling temperature
Q_2	The heat absorbed by the monodentate ligand between evaporation and the T_{DTA} temperature

$$Q_2 = C_p * \Delta T \qquad (III)$$

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C_p	Temperature difference between the boiling temperature of the monodentate ligand and the T_{DTA} temperature
$\Delta Q_{crystal}$	Bond energy difference between the binuclear (I) and mononuclear (II) states
$\Delta Q_{crystal}$	$= E_{bond\ I} - E_{bond\ II}$ (IV)
ΔH_b	Coordinative bond energy

Complex coordination in both states is sqaure planar and the ligand around the metal is the same. Only in state (II) there is one monodentate ligand in the structure (NH_3, H_2O, Et_2NH). With this consideration we accept that $E_{bond\ I}$ and $E_{bond\ II}$ energies are about equal. We have to make this assumption since there are no available methods to measure the E_{bond} energies and moreover no theoretical calculations are given.

$$\Delta Q_{crystal} = 0$$

With this assumption Q_1 and Q_2 can be calculated and Q is the heat directly measured by DSC.

In this study three ligands have been used. These are two ONO type an done ONNO type multidentate Schiff bases. These Schiff bases are N-(2-hydroxyphenyl)salicylaldimine ($SAPH_2$), N-(2-hydroxyphenyl)-2-hydroxy-1-naphthaldimine ($NAPH_2$) and Bis-N,N′-(salicylidene)-1, 3-propanediamine (LH_2).

The open formulas of the prepared complexes with and without the addition of a monodentate ligands are given in Fig. 1.

The elemental analysis of the prepared complexes were made by IR spektroscopy and thermogravimetry. The temperature level at which the monodentate ligand to leave the structure was determined using TG-DTA and the endothermic heat within this level was determined by DSC. Using this heat value coordination bond energy was calculated from Eq. I. Molecular models of some of the prepared complexes have been determined using X-ray diffraction methods and have been published in literature [7–11].

Experimental

The complexes were prepared according to the methods indicated in literature [6–9]. Schiff bases were prepared from the related carbonyl and amine components in EtOH media with condensation reaction and recrystallized in MeOH.

$SAPH_2$: From salicylaldehyde and 2-hydroxy aniline with a 1:1 mole ratio,

$NAPH_2$: From 2-hydroxy-1-naphtaldehyde and 2-hydroxy aniline with a 1:1 mole ratio

LH_2: From salicylaldehyde and 1,3-propanediamine with a mole ratio 2:1

Preparations of NiSAP · NH_3, NiSAP · Et_2NH and NiNAP · Et_2NH: 0.002 mole $SAPH_2$ or $NAPH_2$ was dissolved in 100 mL EtOH:dioxane (1:1) with constant stirring and heating. In this solution were added a solution of

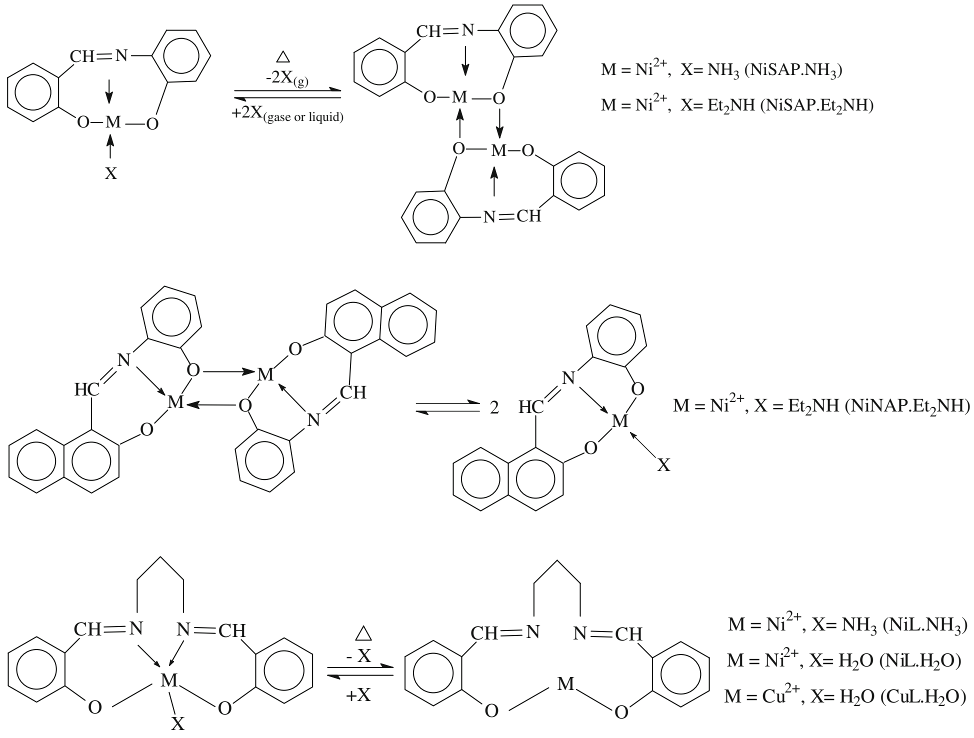

Fig. 1 The open formulas of the prepared complexes with and without the addition of a monodentate ligands

0.002 mole [$NiCl_2(H_2O)_6$] in 20 mL hot MeOH and related monodentate ligand (5 mL concentrated ammonia or 1.5 mL diethylamine). The mixture was heated to the boiling point and was set a side for 24–28 h. The Brown complex crystals were filtered and washed with a small amount of EtOH and dried in air.

Preparation of NiL · NH_3: This green complex was obtained according to the preparation above with LH_2, [$NiCl_2(H_2O)_6$] and ammonia.

Preparations of NiL · H_2O and CuL · H_2O: These complexes were obtained in two steps. About 0.01 mole LH_2 was dissolved in 60 mL EtOH with heating. To this solution were added a solution of 0.01 mole [$NiCl_2(H_2O)_6$] or 0.01 mole [$CuCl_2(H_2O)_6$] in 40 mL hot water and 2 mL triethylamine. The mixture was left to stanf for 2–3 days. After this period NiL or CuL crystals were collected and dried at 100 °C. About 0.002 mole NiL or CuL complexes were dissolved in 80 mL EtOH with heating. To this solution was added 10–20 mL hot water and the mixture was left to stand for 5–12 days. After this period the green crystals of NiL · H_2O or CuL · H_2O were filtered and dried in air.

Elemental analysis results and some important IR values relating to the complexes are given in Table 1. Copper and nickel analysis were made with the GBC Avanta PM model Atomic Absorbtion Spectroscopy, C, H, N analysis were made with Leco 932 CHNS Analyzer equipment. Schimadzu DTG-60H was used for thermogravimetric analysis. Mass loss amounts following the seperation of the NH_3, H_2O and Et_2NH ligands from the complex are given in Table 2. The endothermic heat obtained from these mass losses was measured in Al pan on the Schimadzu DSC-60. All thermogravimetric analysis were made under nitrogen atmosphere at a heating rate of 10 °C min^{-1}. DSC measurements were made under nitrogen atmosphere at heating rate of 5 and 10 °C min^{-1}. ΔH_b, Cp values for H_2O, NH_3 and Et_2NH ligand were taken from literature [10–12]. Every DSC measurement was repeated at least 5 times with a confidence level of 95%.

Results and discussion

Elemental analysis results and some important IR datas as well as metal-monodental ligand bond lengths relating to the five complexes that have been prepared are given in Table 1. These complexes have been prepared according to the information provided in literature. Molecular models of these complexes obtained by X-ray diffraction methods are also given in literature. The mass losses obtained by TG are the expected values. The thermoanalytical data are given in Table 2. The recommended calculation method has been used for the coordinative DMF molecules and appropriate results were obtained [11, 12]. The coordinative bond energies found for the main complex are given in Table 3 together with the values of Eq. I. NiSAP · NH_3, NiSAP · Et_2NH and NiNAP · Et_2NH, which are complexes prepared with N-(2-hydroxyphenyl) salicylaldimine (SAP) and N-(2-hydroxyphenyl)-2-hyrdroxy-1-naphthaldimine (NAP), are diamagnetic with square planar coordination sphere [8–10].

Table 1 Elemental analysis results and some important IR values relating to the complexes

Complex	Elemental analysis (M: Ni^{2+} or Cu^{2+})								IR data (cm^{-1})						
	Expected (%)				Obtained (%)				$\upsilon_{N–H}$	$\upsilon_{C–H\ (Ar)}$	$\upsilon_{C–H\ (Aliph)}$	$\upsilon_{C=N}$	$\upsilon_{C=C\ (ring)}$	δ CH_2	$\delta_{C–H\ (Ar)}$
	C	H	N	M	C	H	N	M							
NiSAP · NH_3	54.42	4.21	9.76	20.46	54.81	5.17	9.88	21.12	3,140 3,240 3,330	3,024 3,047	–	1,614	1,600	1,473	759
NiSAP · Et_2NH	59.52	5.88	8.16	17.11	59.94	5.92	8.27	17.18	3,244	3,018 3,041	2,861 2,934	1,617	1,598	1,474	757
NiNAP · Et_2NH	64.16	5.64	7.12	14.93	63.84	5.55	7.65	14.73	3,342	3,031 3,057	2,863 2,930	1,615	1,597	1,468	757
NiL · H_2O	57.19	5.08	7.84	16.44	56.70	5.17	7.54	15.79	–	3,027 3,055	2,854 2,921	1,629	1,599	1,474	756
CuL · H_2O	56.45	5.01	7.74	17.56	56.17	4.48	8.12	17.16	–	3,024 3,054	2,851 2,923	1,626	1,601	1,471	755
NiL · NH_3	57.35	5.37	11.80	16.49	57.41	5.64	10.96	17.04	3,142 3,249 3,317	3,025 3,055	2,851 2,921	1,628	1,601	1,473	759

Table 2 Thermoanalytical data relating to the complexes

Complex	First thermal reaction			Second thermal reaction		NiO (%) or CuO (%) found over 923 K	
	Dissociation temperature range of monodentate ligands (K)	Mass loss percentage of monodentate ligand		Temp. Range (K)	Mass loss percentage at second thermal reaction		
		Expected	Found			Expected	Found
NiSAP · NH_3 (286,7 g $mole^{-1}$)	480–577	5.93	6.04 ± 0.17	747–835	75.67	26.06	24.91 ± 0.84
NiSAP · Et_2NH (342,7 g $mole^{-1}$)	427–470	21.30	21.92 ± 0.27	738–803	62.24	21.79	22.86 ± 1.23
NiNAP.Et_2NH (392,7 g $mole^{-1}$)	420–483	18.59	18.66 ± 0.42	715–795	55.45	19.06	20.84 ± 1.17
NiL.H_2O (356,7 g $mole^{-1}$)	321–383	5.05	5.25 ± 0.19	583–791	77.44	20.94	21.36 ± 1.45
CuL · H_2O (361,54 g $mole^{-1}$)	351–383	4.98	5.12 ± 0.24	578–617	39.87	22.00	22.32 ± 0.96
NiL · NH_3 (355,7 g $mole^{-1}$)	377–443	4.78	5.01 ± 0.26	598–667	40.72	21.00	21.91 ± 1.62

The dissociation energies for NH_3 and Et_2NH are close to one another at the order of NiSAP · NH_3>NiSAP · Et_2NH>NiNAP · Et_2NH. This is an expected result as the coordinated atom is nitrogen and the steric structure of Et_2NH is larger than NH_3. Et_2NH has a larger molecular volume than NH_3, therefore the length of the bond that it makes with Ni^{2+} ion is longer compared to the bond of Ni–NH_3 [9].

The case is similar for the NiL · H_2O, CuL · H_2O and NiL · NH_3 complexes prepared with Bis-N,N′(salicylidene)-1,3-propanediamine (LH_2). It has not been possible to obtain the NiL · NH_3 complex in the form of a suitable single crystal. Therefore its molecular model cannot be found in literature. However the molecular models of NiL · H_2O and CuL · H_2O are available. The bond energies for the dissociation of NH_3 and H_2O molecules from the complex have been found to be NiL · NH_3>NiL · H_2O>CuL · H_2O. It is not possible to make a direct comparison of NH_3 and H_2O. In the spectrochemical series NH_3 is a much more stronger ligand than H_2O. Therefore it is normal to find the bond energy of NiL · NH_3 higher than the bond energy of NiL · H_2O. The bond energies of NiL · H_2O and CuL · H_2O are comparable, the only difference in these complexes is the central ion. The attraction force formed between the central ion and H_2O is the strength of the bond. For both of these complexes bond lengths can be explained by bond energies. Cu–O bond length in CuL · H_2O has been reported as 2,309 A° and the bond length of Ni–O in NiL · H_2O as 2,015 A°. Therefore Ni–OH_2 bond is shorter and stronger. As it will be noticed, the temperature level where the monodentate ligand dissociates from the complex is also a measure for the bond strength. The higher is the bond energy, the higher is the dissociation temperature will be. Temperature level of the thermal reaction for the dissociation of the monodentate ligand and the peak temperature of the DTG peak for this reaction are given in Table 3. TG-DTA and DSC curves for the complexes are seen in Fig 2a–f and Fig 3a–d respectively. It is clear that the thermal reaction is the mass loss of monodentate ligand as it is in full accordance with the expected mass loss of monodentate ligand.

There is no result found in literature for similar kind of calculations on bond energies determined via thermal analysis. In the given studies in literature, metal-carbonyl bond energies and some metal-ligand bond energies are determined experimentally, via mass spectroscopy, photoelectron spectroscopy and photothermal spectroscopy [13–18]. The results taken from the forementioned studies are comparable with the results given in Table 3.

Theoretical calculations about this subject are more commonly found in literature than the experimental results and there is no significant difference between the experimental results and theoretically calculated values [19–21].

There are many publications about the thermal decomposition of Ni^{2+} and Cu^{2+} complexes with similar tridentate and tetradentate Schiff base ligands. These studies have been made under inert atmosphere and it has been reported that the complex turns into metal oxide at around 650 °C. No monodentate ligands have been used together with any Schiff base in the complexes in these studies [22, 23]. Therefore the thermal reaction is the degradation of organic part of the complex. On the TG curves it is not

Table 3 Calculated bond energies of the complexes via DSC results and thermodynamic data

Complex	Average temperature range of mass loss of monodentate ligands (K)	Evaporation temperature of monodentate ligands at 1 atm (J mole^{-1})	Q_1 Cp*ΔT (liquid phase; J mole^{-1})	Q_2 Cp*ΔT (gas phase; J mole^{-1})	Heat values by DSC (kJ mole^{-1})	Calculated coordinative bond energy (kJ mole^{-1})	Average bond energy at 95% confidence level (kJ mole^{-1})
NiSAP · NH_3	561.51	23,255		34.43	59.51	25.08	22.35 ± 2.46
				35.78	59.38	23.60	
				35.48	55.98	20.50	
				35.43	56.04	20.61	
				35.38	56.64	21.98	
NiSAP · Et_2NH	508.13	28,171.78	5,607.58	25.22	88.74	29.74	26.89 ± 2.94
				27.30	88.92	24.84	
				36.59	84.02	23.65	
				29.04	87.44	24.62	
				19.56	82.25	28.91	
				19.74	83.09	29.57	
NiNAP · Et_2NH	483.33	28,171.78	5,607.58	21.91	71.92	16.23	20.07 ± 3.71
				21.09	78.08	23.21	
				21.72	75.21	19.71	
				24.41	81.09	22.90	
				25.44	77.51	18.29	
NiL · H_2O	375.94	40,656	6,033.64	30.42	53.11	6.39	6.16 ± 0.51
				84.02	52.50	5.72	
				3.62	53.70	7.01	
				826.04	53.52	6.00	
				19.56	52.02	6.09	
				19.74	51.67	5.74	
CuL · H_2O	360.13	40,656	4,904.982	718.39	48.32	2.04	1.97 ± 0.18
				748.80	48.25	1.94	
				748.44	48.05	1.74	
				797.44	48.39	2.03	
				665.24	48.34	2.11	
NiL · NH_3	426.32	23,255		5.50	29.05	10.24	9.96 ± 1.64
				5.81	29.06	9.20	
				5.69	28.94	10.44	

possible to clearly determine the structure of the molecules seperated by degradation from the TG curves. In this study on the other hand there is a small monodentate ligand besides the Schiff base ligand. In our TG studies dissociation of this monodentate ligand from the structure is clearly seen as the first thermal reaction. The second thermal reaction observed on the TG curves is the degradation of the Schiff base in parallel to the studies mentioned in literature.

The main handicap in this study is the $\Delta Q_{crystal}$ mentioned in the introduction. The Born-Haber energies corresponding to the states when the monodentate ligand is present or absent in the complex are different. If these values can be ignored in comparison to the other energies the values found in this study are logical. The facts that there are no ionic changes both in absence and presence of the monodentate ligand, that in both cases the complex is fully covalent and that the molecular mass of the seperated ligand is small help strengthen our assumption. This assumption cannot be made for a real ionic complex. Similar studies have been made to this effect with $[NiCl_2(H_2O)_6]$, $[NiCl_2(NH_3)_6]$ and $[NiCl_2(en)_3]$ but the obtained results are not meaningful. From the TG and DSC curves of these compounds the H_2O, NH_3 and ethylenediamine amounts are clearly seen and the absorbed amount of heat is clearly measured. However

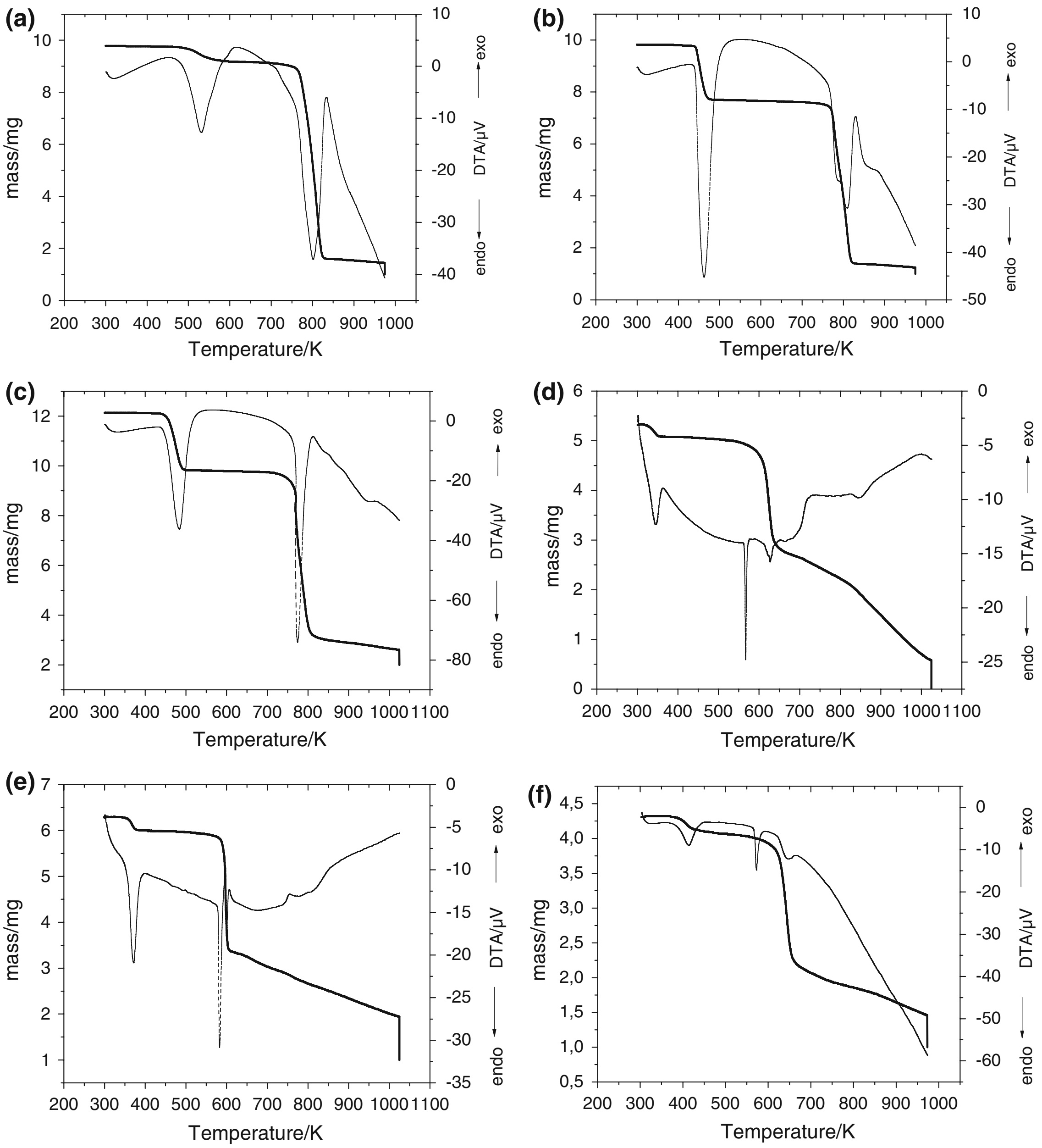

Fig. 2 **a** The TG curve of NiSAP · NH_3. **b** The TG curve of NiSAP · Et_2NH. **c** The TG curve of NiNAP · Et_2NH. **d** The TG curve of NiL · H_2. **e** The TG curve of CuL · H_2O. **f** The TG curve of NiL · NH_3

obtained results are unexplicable. These results are given in Table 4.

These ionic complexes cannot be compared with the complexes given in Table 2 because there are a high number of monodentate ligands such as H_2O, NH_3 in these ionic complexes and also ionic spheres of different states show significant differences. For example in the $[Ni(H_2O)_6Cl_2]$ complex there are 6 H_2O molecules around Ni^{2+} ion. When the H_2O molecules leave the structure thermally, crystal structure of $NiCl_2$ including $Ni^{2+}$and Cl^- ions is left behind. In this case Born-Haber energies of both states cannot be approximated. Indeed the obtained results given in Table 4 do not show the expected order. However the results in Table 3 are meaningful. The obtained coordinative bond energies are normal. They are much lower than covalent bond energies and are at about the same level with hydrogen bond energies. We have not seen any definite data in literature regarding the level of coordination bond value. There are however data regarding the energy levels of hydrogen bonds. Since the

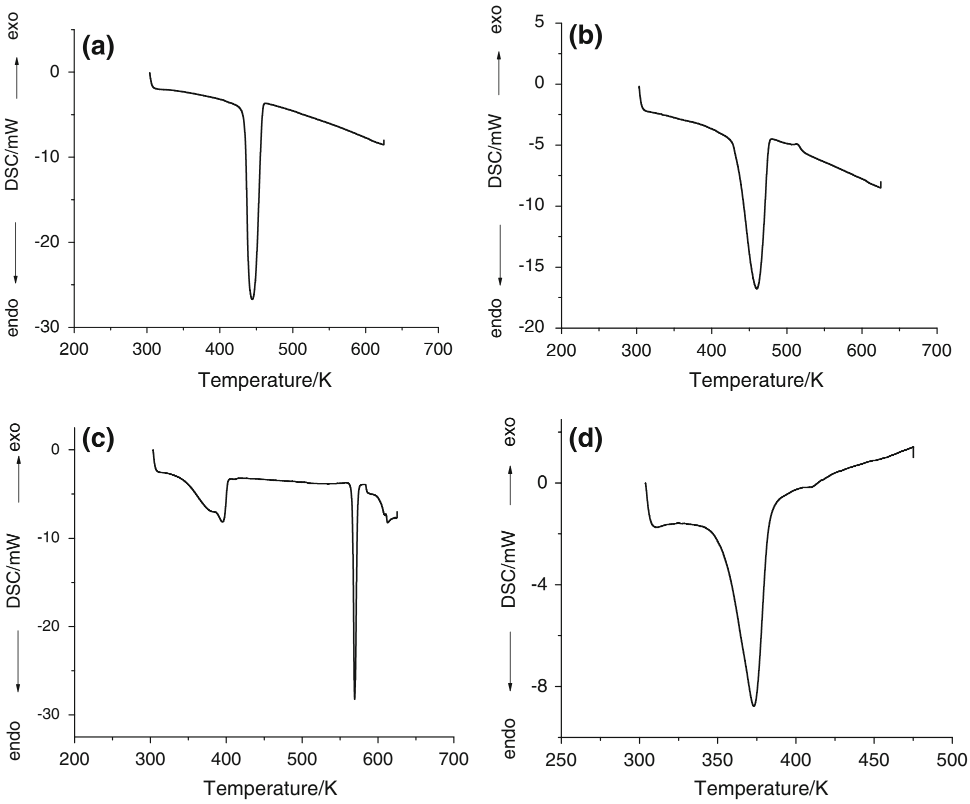

Fig. 3 **a** The DSC curve of NiSAP · Et_2NH. **b** The DSC curve of NiNAP · Et_2NH. **c** The DSC curve of NiL · H_2O. **d** The DSC curve of CuL · H_2O

Table 4 Calculated bond energies of ionic complexes

Complex	Dissociation of all monodentate ligands			Calculated ΔH_{bond} for one monodentate ligand (kJ mole^{-1})
	Temperature range (K)	Number of dissociated monodentate ligands	Calculated ΔH_{bon} (kJ)	
$[NiCl_2(H_2O)_6]$	300–499	6	-68.03 ± 20.10	-10.13 ± 0.73
$[NiCl_2(NH_3)_6]$	335–576	6	83.72 ± 15.95	13.95 ± 2.66
$[NiCl_2(en)_3]$	348–600	3	-61.00 ± 17.58	-20.33 ± 5.86

hydrogen bond level is the highest level of dipole-dipole interaction, these must be comparable with the energies of coordination bonds. The results given in Table 3 provide evidence for this matter.

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