

THERMAL STUDIES OF NICKEL(II) SQUARATE COMPLEXES OF TRIAMINES IN THE SOLID STATE

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Abstract

$[\text{NiL}_2]\text{C}_4\text{O}_4 \cdot n\text{H}_2\text{O}$ [where $n=2$ when L =diethylenetriamine(dien) and N-(3-aminopropyl)-1,3-propanediamine (dpt); $n=3$ when L =N-(2-aminoethyl)-1,3-propanediamine (aepn); $n=0$ when L =N²-methyldiethylenetriamine (medien)] and $\text{Ni}(\text{tmdien})\text{C}_4\text{O}_4 \cdot 2\text{H}_2\text{O}$ (where tmdien =1,4,7 trimethyl-diethylenetriamine) have been synthesised and investigated thermally in the solid state. $\text{Ni}(\text{dpt})\text{C}_4\text{O}_4 \cdot \text{H}_2\text{O}$ has also been synthesised pyrolytically in the solid state from the corresponding bis complex. All the complexes possess octahedral geometry. The squarate anion takes part in coordination only in monotriamine species. $[\text{Ni}(\text{medien})_2]\text{C}_4\text{O}_4$ upon heating undergoes phase transition (270–285°C; $\Delta H=4.9 \text{ kJ mol}^{-1}$) accompanied by colour change pink to grey. Thermal stability decreases with increase in chain length of the triamines.

Keywords: DSC, nickel(II) squarate, phase transition, TG-DTA, triamine

Introduction

Syntheses of triamine complexes of transition and non-transition metals are known [1–7]. Measurements of stability constants and thermochemical studies of triamine complexes in solution reveal that the stability of the complexes decreases as the carbon chain length of the triamine increases (5:5)→(5:6)→(6:6) [8–9]. We reported thermal behaviour of diethylenetriamine(dien), N-(2-aminoethyl)-1,3-propanediamine (aepn) and N-(3-aminopropyl)-1,3-propanediamine (dpt) of nickel(II), zinc(II) and cadmium(II) with counter anions like, Cl^- , Br^- , I^- , SO_4^{2-} , SeO_4^{2-} , NO_3^- , SCN^- etc. [5–7] and observed several novel findings. However, with a counter anion squarate, ($\text{C}_4\text{O}_4^{2-}$) no such report is yet in literature. It is known that $\text{C}_4\text{O}_4^{2-}$ may act as versatile ligand and has very high thermal stability [10–16]. Recently, we reported [17] diamine complexes of nickel(II)

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squarate where novel phase transitions as well as decomposition phenomena along with the syntheses of conformational isomers varying preparative procedure are noticed. Thus triamine complexes of nickel(II) squarate is expected to exhibit some new findings. To study this we choiced five triamines i.e. dien, N^2 -methyldiethylenetriamine(medien), 1,4,7-trimethyldiethylenetriamine (tmdien), aepn, and dpt forming (5:5), (5:5), (5:5), (5:6) and (6:6) membered chelate rings respectively, to see the chain length as well as alkyl substitution effect on the syntheses as well as thermal properties of nickel(II) squarate complexes with these triamines.

Experimental

High purity squaric acid, dien, aepn, dpt, medien, and tmdien were purchased from Aldrich Chemical Company Inc. and used as received. All other chemicals used were of analytical reagent grade. Nickel(II) squarate dihydrate, $(NiC_4O_4 \cdot 2H_2O)$ was prepared according to the procedure described earlier [17]. The thermal analysis (TG-DTA) was carried out on a Shimadzu DT-30 thermal analyser in dynamic atmosphere of nitrogen (flow rate : $30 \text{ cm}^3 \text{ min}^{-1}$). The sample (particle size within 150–200 mesh) was heated in a platinum crucible at a rate of $10^\circ\text{C min}^{-1}$ with inert alumina as reference. The enthalpy change of the phase transition was derived using a Perkin-Elmer DSC-2 differential scanning calorimeter using indium metal as calibrant. The instruments used for recording the IR spectra (KBr disc at ambient), electronic spectra (nujol mull, at ambient), elemental analyses and effective magnetic moments at room temperature (22°C) were as reported earlier [17].

Preparation of the complexes

Triamines were (3–4 mmol) added to finely powdered nickel(II) squarate (1 mmol) and the resulting mixture was kept in stoppered conical flask. After a few days the mixture was treated with water and filtered. On keeping the filtrate in a $CaCl_2$ -desiccator the desired complexes were separated out which was filtered, washed with isopropanol and dried over $CaCl_2$ - desiccator. The following complexes were synthesised : $[Ni(\text{dien})_2]C_4O_4 \cdot 2H_2O$ (1), $[Ni(\text{aepn})_2]C_4O_4 \cdot 3H_2O$ (2), $[Ni(\text{dpt})_2]C_4O_4 \cdot 2H_2O$ (3), $[Ni(\text{medien})_2]C_4O_4$ (4), and $Ni(\text{tmdien})C_4O_4 \cdot 2H_2O$ (5).

$Ni(\text{dpt})C_4O_4 \cdot H_2O$ (6) was prepared by isolation of intermediate species (vide infra) derived upon heating $[Ni(\text{dpt})_2]C_4O_4 \cdot 2H_2O$ (3) (Fig. 2) in the solid state and recrystallising it from water.

Results and discussion

The complexes were recrystallised several times and their purity was assured from their reproducible elemental analyses, magnetic susceptibility, electronic, IR spectra and thermal analyses (TG-DTA). Elemental analyses suggest that among the five triamines only tmdien produces mono species, $Ni(\text{tmdien})C_4O_4 \cdot$

Table I Elemental analyses, magnetic and electronic (nujol) spectral data of triamine complexes of nickel(II) squarate

Complex	Colour	No.	Elemental analyses/% ^a			$\mu_{\text{eff}}/\text{BM}$	$\lambda_{\text{max}}/\text{nm}$
			C	H	N		
[Ni(dien) ₂]C ₂ O ₄ ·2H ₂ O	pink	1	34.8(34.9)	7.6(7.3)	20.5(20.3)	3.1	550, 355
[Ni(aepn) ₂]C ₄ O ₄ ·3H ₂ O	pink	2	36.5(36.6)	7.9(7.8)	18.1(18.3)	3.2	560, 375
[Ni(dpt) ₂]C ₄ O ₄ ·2H ₂ O	pink	3	40.8(40.9)	8.2(8.1)	17.8(17.9)	3.2	555, 380
[Ni(medicn) ₂]C ₄ O ₄	pink	4	41.5(41.5)	7.4(7.4)	20.6(20.7)	3.1	545, 340
Ni(cmdien)C ₄ O ₄ ·2H ₂ O	sky blue	5	37.5(37.5)	6.5(6.5)	11.8(11.9)	3.1	550, 385
Ni(dpt)C ₄ O ₄ ·H ₂ O	sky blue	6	37.4(37.5)	5.7(5.9)	13.0(13.1)	3.1	555, 385

^aPercentages in parentheses are theoretically calculated values

$2\text{H}_2\text{O}$ (5) from solution and dpt produces mono complex, $\text{Ni}(\text{dpt})\text{C}_4\text{O}_4 \cdot \text{H}_2\text{O}$ in solid state (vide infra) whereas the remaining three triamines as well as dpt yield bis species, $[\text{NiL}_2]\text{C}_4\text{O}_4 \cdot n\text{H}_2\text{O}$ (for $L=\text{medien}$, $n=0$; $L=\text{dpt}$ or dien , $n=2$ and for $L=\text{aepn}$, $n=3$) from solution. Steric effect might be responsible for such difference in stoichiometry. Magnetic susceptibility values of all the complexes are typical to octahedral nickel(II) (Table 1) and electronic spectral data also corroborate this (Table 1). IR spectral study reveals that each triamine is chelated in their respective complexes. To determine the coordination mode of $\text{C}_4\text{O}_4^{2-}$ ion, IR spectra at the region of $1400\text{--}1800\text{ cm}^{-1}$ are analysed carefully, since $\text{C}_4\text{O}_4^{2-}$ moiety exhibits characteristic IR bands in its different mode of coordination at that region [15].

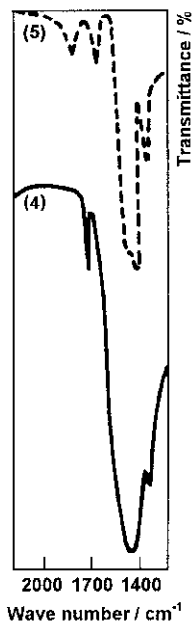


Fig. 1 IR spectra of $[\text{Ni}(\text{medien})_2]\text{C}_4\text{O}_4$ (4) (—) and $\text{Ni}(\text{tmdien})\text{C}_4\text{O}_4 \cdot 2\text{H}_2\text{O}$ (5) (- - -)

It is observed that all the bis species exhibit a very strong and broad band at ~ 1520 to $\sim 1540\text{ cm}^{-1}$, assigned to a mixture of C–C and C–O stretching vibration of squarate ligand (Fig. 1). In addition to that only one sharp band at $\sim 1710\text{ cm}^{-1}$ assigned to C=O (Fig. 1) is observed in all bis complexes. In case of mono species, the IR band assigned to mixture of C–C and C–O stretching vibrations of squarate ligand shifts towards lower wave number region (Fig. 1) ($\sim 1470\text{ cm}^{-1}$). The high energy band ($\sim 1710\text{ cm}^{-1}$) obtained in case of bis species becomes weakened and two additional bands at ~ 1620 and $\sim 1750\text{ cm}^{-1}$ (Fig. 1) appear indicating all four oxygen atoms are not in the same environment [16]. From the above it can be considered that in mono species, squarate ion is coordinated but

not in bis species. Thus the bis species should possess N_6 chromophore around nickel(II). The mono species, **5** and **6** contain one and two molecules of water respectively per molecule of the complexes. Their magnetic and electronic spectral data are typical to octahedral nickel(II) (Table 1). Both the species exhibit alike IR spectral patterns assigned to squarate ligand. Thus mode of coordination of squarate ligand is same in both of them. Now, from the chemical composition of complex **6** it is assumed that the tridentate amine, bidentate squarate anion and monodentate water molecule are around nickel(II) making the chromophore N_3O_3 , $[\text{Ni}(\text{dpt})\text{C}_4\text{O}_4\cdot\text{H}_2\text{O}]$ to attain octahedral geometry. Based on this proposition the tentative structure of complex **5** should be $[\text{Ni}(\text{tmdien})\text{C}_4\text{O}_4\cdot\text{H}_2\text{O}]\cdot\text{H}_2\text{O}$.

Simultaneous TG-DTA analyses reveal that the bis species, $[\text{NiL}_2]\text{C}_4\text{O}_4\cdot n\text{H}_2\text{O}$ ($n=2$ for $L=\text{dien}$ or dpt ; $n=3$ for $L=\text{aepn}$ and $n=0$ for $L=\text{medien}$) upon heating lose the respective water molecules in a single step yielding $[\text{NiL}_2]\text{C}_4\text{O}_4$ without showing any colour change (Fig. 2). All the dehydrated species revert on exposure to humid atmosphere. $[\text{Ni}(\text{dpt})_2]\text{C}_4\text{O}_4$ on further heating starts decomposing at $\sim 132^\circ\text{C}$ with the formation of intermediates, $\text{NiL}_{1.5}\text{C}_4\text{O}_4$ and NiLC_4O_4 as is evident from its TG-curve (Fig. 2).

We tried to synthesise both the intermediates derived in the solid state in pure form through crystallisation but succeeded to isolate $\text{Ni}(\text{dpt})\text{C}_4\text{O}_4\cdot\text{H}_2\text{O}$ (**6**) only. All other bis complexes, **1**, **2** and **4** decompose at ~ 290 , ~ 250 , and $\sim 315^\circ\text{C}$ respectively and do not show any complex species as an intermediate. None of the bis species show thermally induced phase transition, except $[\text{Ni}(\text{medien})_2]\text{C}_4\text{O}_4$ (**4**) which undergoes an irreversible endothermic phase transition ($270\text{--}285^\circ\text{C}$; $\Delta H=4.9\text{ kJ mol}^{-1}$) accompanied with colour change pink to grey (**4** \rightarrow **4a**; Fig. 4). The species **4a** reverts immediately after cooling to ambient temperature. Here

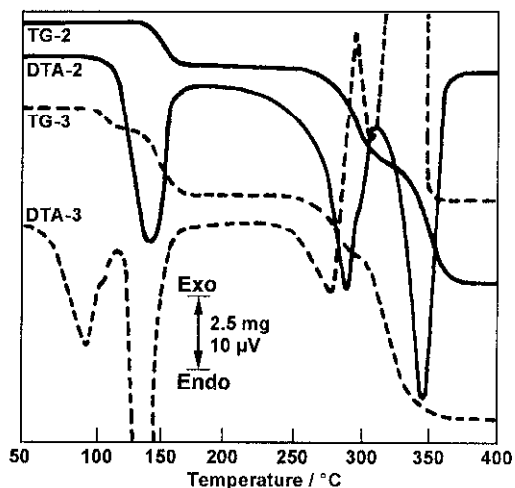


Fig. 2 TG-DTA curves of $[\text{Ni}(\text{aepn})_2]\text{C}_4\text{O}_4\cdot 3\text{H}_2\text{O}$ (**2**) (sample mass 12.44 mg) (—) and $[\text{Ni}(\text{dpt})_2]\text{C}_4\text{O}_4\cdot 2\text{H}_2\text{O}$ (**3**) (sample mass 14.27 mg) (---)

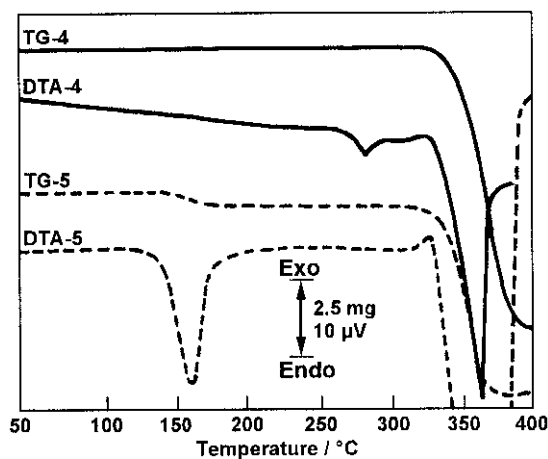


Fig. 3 TG-DTA curves of $[\text{Ni}(\text{medien})_2]\text{C}_4\text{O}_4$ (4) (sample mass 12.06 mg) (—) and $\text{Ni}(\text{tmdien})\text{C}_4\text{O}_4 \cdot 2\text{H}_2\text{O}$ (5) (sample mass 9.60 mg) (---)

the probability of the occurrence of configurational isomerisation does not arise considering the coordination environment around nickel(II). On the other hand the transition is either due to conformational changes in the triamine chelate rings [5b, 5d, 6b, 7b] or geometrical isomerisation [5a] (e.g. sym. fac \rightarrow mer). The characterisation of **4a** could not be done due to lack of instrumental facility although the value of enthalpy change (**4** \rightarrow **4a**; 4.9 kJ mol^{-1}) suggests conformational isomerisation as it is close to those values reported earlier [5b, 5d, 6b, 7b]. The mono species, $\text{Ni}(\text{tmdien})\text{C}_4\text{O}_4 \cdot 2\text{H}_2\text{O}$ (**5**) upon heating loses two molecules of water in single step in the temperature range 130–180°C. And the $\text{Ni}(\text{dpt})\text{C}_4\text{O}_4 \cdot \text{H}_2\text{O}$ (**6**) also loses water molecule in one step in the temperature range 120–160°C. Both the dehydrated species retain the identity in colour and their temperature range for dehydration hints the presence of coordinated water molecule in them. The dehydrated species revert in humid atmosphere as a result their characterisation could not be done. It is interesting to note that IR spectral bands responsible for triamine ligand of the dehydrated species derived from **5** and **6** shift slightly from their respective parent complexes. On the other hand such type of shift is not visible in the case of hydrated bis triamine complexes. The shifting in spectral bands probably arises due to the release of interaction of water molecule with amine ligand.

The squarate anion may generate hydrogen bonding with the amine hydrogens. From our previous experience it may be inferred that on thermal excitation breaking/weakening of such hydrogen bonds may lead to phase transitions. In the present case only $[\text{Ni}(\text{medien})_2]\text{C}_4\text{O}_4$ shows thermochromism though actual cause behind the phase transition is unexplored (vide supra). Again high thermal stability of the squarate moiety hints the possibility of formation of novel intermediates on thermal agitation. Here only $[\text{Ni}(\text{dpt})_2]\text{C}_4\text{O}_4$ produces mono species,

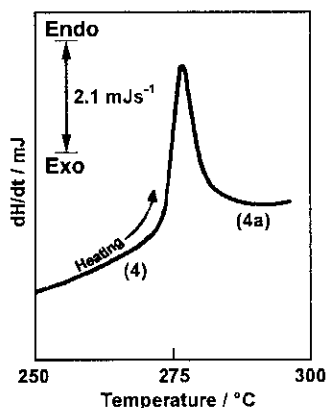


Fig. 4 DSC curves of $[\text{Ni}(\text{medien})_2]\text{C}_4\text{O}_4$ (4) (sample mass 10.04 mg) (—)

which could not be prepared from solution. It is reported [7b] that thermal stability of triamine complexes of nickel(II) decreases with increase in the chain length of triamines (5:5→5:6→6:6). The same trend prevailed in squarate system though substitution effect is not so visible.

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