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SYNTHESES AND SPECTROTHERMAL STUDIES OF TRIETHANOLAMINE COMPLEXES OF Co(II), Ni(II), Cu(II) AND Cd(II) SQUARATES

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The triethanolamine complexes, $[M(tea)_2]sq \cdot nH_2O$, (n=2 for Co(II), n=0 for Ni(II), Cu(II) and n=1 for Cd(II), *tea*=triethanolamine, sq^{2-}=squarate), have been synthesized and characterized by elemental analyses, magnetic susceptibility and conductivity measurements, UV-Vis and IR spectra, and thermal analyses techniques (TG, DTG and DTA). The Co(II), Ni(II) and Cu(II) complexes possess octahedral geometry, while the Cd(II) complex is monocapped trigonal prismatic geometry. Dianionic squarate behaves as a counter ion in the complexes. The thermal decomposition of these complexes takes place in three stages: (*i*) dehydration, (*ii*) release of the tea ligands and (*iii*) burning of organic residue. On the basis of the first DTG_{max} of the decomposition, the thermal stability of the anhydrous complexes follows the order: Ni(II), 289ºC>Co(II), 230ºC>Cd(II), 226ºC>Cu(II), 170ºC in static air atmosphere. The final decomposition products – the respective metal oxides – were identified by FTIR spectroscopy.

Keywords: *squaric acid, thermal decomposition, triethanolamine complexes*

Introduction

Squaric acid, (3,4-dihydroxycyclobut-3-ene-1,2-dione, $H_2C_4O_4$, H_2sq, Fig. 1a), synthesized for the first time by Cohen *et al*. in 1959 [1], has been of much interest because of its cyclic structure and possible aromaticity. The behavior of the squarate dianion has been thoroughly investigated in the last years both in solution [2–4] and in the solid-state [5–27]. The squarate anion does not behave like a chelating ligand but rather like a bridge between two or more metal atoms as mono- or bidentate ligand. The squarato mononuclear complexes with first-row transition metal ions are isolated when squarate acts as a monodentate ligand [16, 18] whereas dinuclear and chain compounds result when the squarato ligand is coordinated in μ-1,2- [14, 15, 25–27] and μ-1,3-*bis*-monodentate [4–8, 13, 16, 28, 29] fashions. Diaqua and tetraaqua complexes of sq with transition metals were reported [5–8]. Synthesis and structural characterization of mixed-ligand transition metal complexes of sq with mono- and bidentate N-donor ligands such as pyridine [12], imidazole [13], 2,2'-bipyridine [13–17] and 1,10-phenanthroline [15–18] appear in recent literature. In some transition metal complexes, the squaric acid acts as a counter ion [19–24]. Solid-state thermal studies of several metal squarate and mixed ligand of the metal squarate complexes have been reported, indicating a high thermal stability of the squarate moiety [30–34].

The triethanolamine ligand, (tris(2-hydoxyethyl)amine, $N(CH_2CH_2OH)_3$, Fig. 1b) has a number of potential donor sites which are high in electronegativity, and a diversity of coordination modes. Although, tea usually acts as a N,O,O'-tridentate ligand in transition metal complexes [35–37], a N,O,O',O''-tetradentate ligand behavior has also been observed, especially towards metal ions having large ionic radii [38–40]. Yılmaz *et al*. has studied [41] the thermal decomposition of the tea complexes of metal saccharinates, while the decomposition behaviours of the aqua complexes of the metal(II) squarates were studied by Bailey *et al*. [42].

We reported earlier the crystal structure determinations of the $[Ni(tea)_2]sq$, $[Cu(tea)_2]sq$ and $[Cd(tea)_2]sq \cdot H_2O$ complexes [20–22]. The Ni(II), Cu(II) and Cd(II) complexes crystallize in the triclinic, monoclinic and triclinic system with space group $P\bar{1}$, $P2_1/c$, $P\bar{1}$, respectively. Two tea ligands coordinate to the Ni(II) and Cu(II) ions through four O atoms and two N atoms acting as N,O,O'-tridentate ligands, resulting in a distorted octahedral environment. In the complex cation, in which the Cd(II) ion is

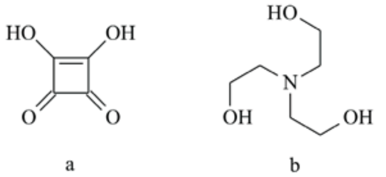

Fig. 1 a – Squaric acid and b – triethanolamine

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coordinated by two tea ligands and seven-coordinated, both tri- and tetradentate tea molecules are present. One of the tea ligands acts as an N,O,O'-tridentate ligand, whereas the other behaves as an N,O,O',O''-tetradentate donor. The squarate anions and $[M(tea)_2]^{2-}$ cations are linked to each other by hydrogen bonding between coordinated hydroxyl H atoms of tea and squarate O atoms, forming layers.

In the present paper, syntheses, spectroscopic properties and thermal decomposition of the Co(II), Ni(II), Cu(II) and Cd(II) complexes with squaric acid and triethanolamine are reported.

Experimental

Materials and instrumentation

All chemicals used were analytical reagent products. Elemental analyses for C, H and N were carried out at the Tübitak Marmara Research Centre in Turkey. Magnetic susceptibility measurements at room temperatures were performed using a Sherwood Scientific MXI model Gouy magnetic balance. UV-Vis spectra were obtained for the aqueous solutions (10^{-3} M) of the complexes with a Unicam UV2 spectrometer in the range 900–190 nm. IR spectra were recorded in the 4000–500 cm^{-1} region with a Mattson 1000 FT-IR spectrometer using KBr pellets. Thermal analysis curves (TG, DTG and DTA) were recorded simultaneously in a static air atmosphere with a Rigaku TG8110 thermal analyzer. The heating rate was 10ºC min^{-1} and the DTG sensitivity was 0.05 mg s^{-1}. The conductance values were measured on 522 Crison conductimeter.

Synthesis of the complexes

A solution of squaric acid (0.57 g, 5 mmol) in distilled water (20 mL) was neutralized with NaOH (0.40 g, 10 mmol) and added dropwise with stirring at 60°C to a solution of $MCl_2 \cdot xH_2O$ (5 mmol; M=Co(II), 1.185 g; Ni(II), 1.185 g; Cu(II), 0.850 g, Cd(II), 0.917 g; x=7, 7, 2 and 0, respectively) in distilled water (20 mL). The mixture was stirred for 4 h at 60°C and then cooled to room temperature. The $Msq \cdot 2H_2O$ crystals formed were filtered and washed with 10 mL of cold distilled water and dried in air.

A solution of triethanolamine (0.596 g, 4 mmol) in methanol (20 mL) was added dropwise with stirring to a suspension of $Msq \cdot 2H_2O$ (2 mmol; M=Co(II), 0.414 g; Ni(II), 0.414 g; Cu(II), 0.423 g; Cd(II), 0.520 g) in water (30 mL). The mixture was stirred at 60ºC for 12 h and then cooled to room temperature. The crystals formed were filtered and washed with 10 mL of water and methanol and dried in air.

Results and discussion

Structures of the complexes

Analytical results, molar conductivity values and compositions of the complexes are listed in Table 1. The complexes were synthesized in good yields and with high purity. The Ni(II), Cu(II) and Cd(II) complexes of sq with tea were also structurally characterized [20–22]. The elemental analyses conformed to their given formula (Table 1). The molar ratio M:tea:sq in all the complexes are 1:2:1. In the Co(II), Ni(II) and Cu(II) complexes, tea acts as a tridentate ligand (N,O,O'), while in the Cd(II) complex, which is seven coordination, tea ligand behaves both tridentate (N,O,O') and tetradentate (N,O,O',O'') [20–22]. Dianionic squarate behaves as a counter ion in all the complexes. These results were supported by conductivity measurements. The molar conductance values (Λ) of the complexes are 167, 206, 151 and 187 S cm^2 mol^{-1} for the Co(II), Ni(II), Cu(II) and Cd(II), respectively, indicating that all the complexes are a 1:2 electrolyte in water.

UV-Vis spectra and magnetic moments of the complexes

The λ_{max}, ε, 10 Dq and effective magnetic moment values and assignment of *d–d* transitions of the complexes are given in Table 2. The Co(II), Ni(II) and Cu(II)

Table 1 Analytical data and conductance values of the complexes

Complexes	$F.W.$/g mol^{-1}	Found (calc.)/%			Yield/%	Colour	Λ/S cm^2 mol^{-1}
		C	H	N			
$[Co(tea)_2]sq \cdot 2H_2O$ $C_{16}H_{34}N_2O_{12}Co$	505.38	37.78 (38.03)	7.02 (6.78)	5.55 (5.54)	65	brown	167
$[Ni(tea)_2]sq$ $C_{16}H_{30}N_2O_{10}Ni$	469.11	40.98 (40.97)	6.53 (6.45)	5.98 (5.97)	60	blue	206
$[Cu(tea)_2]sq$ $C_{16}H_{30}N_2O_{10}Cu$	473.98	40.16 (40.55)	6.52 (6.38)	5.83 (5.91)	63	green	151
$[Cd(tea)_2]sq \cdot H_2O$ $C_{16}H_{32}N_2O_{11}Cd$	540.85	35.43 (35.53)	6.00 (5.96)	4.98 (5.18)	55	colourless	187

Table 2 Absorption spectra and magnetic moment values of the complexes

Complexes	λ_{max}/nm	ε/L cm^{-1} mol^{-1}	Assignment of *d–d* transitions	10 Dq/cm^{-1}	μ_{eff}/BM
[Co(tea)$_2$]sq·2H$_2$O	530	48	$^4T_{1g}\rightarrow{}^4T_{1g}$ (P)	–	4.21
[Ni(tea)$_2$]sq	388 641 890	81 35 23	$^3A_{2g}\rightarrow{}^3T_{1g}$ (P) $^3A_{2g}\rightarrow{}^3T_{1g}$ $^3A_{2g}\rightarrow{}^3T_{2g}$	11236	2.61
[Cu(tea)$_2$]sq	741	119	$^2E_g\rightarrow{}^2T_{2g}$	13495	1.84

complexes exhibit the magnetic moment values of 4.21, 2.61 and 1.84 BM, which correspond to three, two and one unpaired electrons, respectively, which are consistent with a weak field octahedral geometry. The Cd(II) complex is diamagnetic as expected.

The tea ligand and sq^{2-} anion exhibit two bands in the UV region at 211 and 229 nm, which are assigned to $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ transitions and the bands with low intensity between 350 and 800 nm are due to *d–d* transitions. The assignments of d-d transitions corresponded to an octahedral coordination geometry of the metal ions and the values of the 10 Dq parameter were found using Tanabe and Sugano diagrams [43].

The λ_{max} value of the absorption band in the spectrum of the Co(II) complex is 530 nm and the corresponding ε value is 48 L mol^{-1} cm^{-1}. The λ_{max} value was assigned to the $^4T_{1g}\rightarrow{}^4T_{1g}$ (P) *d–d* transition, which is characteristic of octahedral geometry around the metal ion [44]. The $^4T_{1g}\rightarrow{}^4T_{2g}$ and $^4T_{1g}\rightarrow{}^4A_{2g}$ transition was not observed which is of low and high energy, respectively, and the $^4T_{1g}\rightarrow{}^4T_{2g}$ shifts to the IR region, while $^4T_{1g}\rightarrow{}^4A_{2g}$ shifts to the UV region and hidden under the intraligand transitions in the spectrum. Therefore, the 10 Dq value for Co(II) complex could not be calculated.

The UV-Vis spectrum for [Ni(tea)$_2$]sq exhibits three weak *d–d* absorption transitions centered at 388 nm (ε=81 L mol^{-1} cm^{-1}), 641 nm (ε=35 L mol^{-1} cm^{-1}) and 890 nm (ε=23 L mol^{-1} cm^{-1}) and supported octahedral geometry. These values were assigned to $^3A_{2g}\rightarrow{}^3T_{1g}$ (P), $^3A_{2g}\rightarrow{}^3T_{1g}$ and $^3A_{2g}\rightarrow{}^3T_{2g}$, respectively. The 10 Dq value for the Ni(II) complex was calculated as 11236 cm^{-1}.

The single band observed for the complex of copper(II) at 741 nm (ε=119 L mol^{-1} cm^{-1}) that all three transitions, i.e. $^2B_{1g}\rightarrow{}^2E_g$, $^2B_{1g}\rightarrow{}^2B_{2g}$ and $^2B_{1g}\rightarrow{}^2A_{1g}$ lie within one broad envelope. The 10 Dq value for the complex was calculated as 13495 cm^{-1}.

The colourless Cd(II) complex do not show any *d–d* bands as expected but only exhibits the intraligand transitions.

IR spectra

The main IR group frequencies of the metal complexes are presented in Table 3. The strong bands at 3357, 3385, 3356 and 3391 cm^{-1} in the spectra of the Co(II), Ni(II), Cu(II) and Cd(II) complexes, respectively, are assigned to ν_{OH} stretching of the ethanol groups of the tea ligand. ν_{OH} stretching of water molecule appears at 3462 and 3496 cm^{-1} of the Co(II) and Cd(II) complexes, respectively. The weak peaks in the 3081–2803 cm^{-1} range are due to ν_{CH} stretching of tea. A very strong and broad absorption centered at 1497, 1424; 1499, 1433; 1501, 1413 and 1511, 1437 cm^{-1} of the Co(II), Ni(II), Cu(II) and Cd(II) complexes, respectively, are assigned to the combination of squarato C–O and C–C band stretching vibrations, respectively. In addition to that only one weak peak at around 1715 cm^{-1} assigned to C=O is ob-

Table 3 IR group frequencies (cm^{-1})

Complexes	ν_{OH}	$\nu_{OH_{tea}}$	ν_{CH_2}	$\nu_{C=O}$	$\nu_{C=C}$	$\nu_{C-C}+\nu_{C-O}$
Squaric acid	3462s	–	–	1818w	1618m	1530vs,b 1516s
[Co(tea)$_2$]sq·2H$_2$O	3462s	3357s	3023m 2859m	1725w	–	1497vs,b 1424s
[Ni(tea)$_2$]sq	–	3385s	3031m 2981m	1737w	–	1499vs,b 1433s
[Cu(tea)$_2$]sq	–	3356s	3081m 2982m	1705w	–	1501vs,b 1413s
[Cd(tea)$_2$]sq·H$_2$O	3496m	3391m	2943w 2803w	1712w	–	1511vs,b 1437s

w – weak, m – medium, s – strong, vs – very strong and b – broad.

served due to $C_4O_4^{2-}$ ion acts as a counter anion in the complexes [30–34]. These stretching vibrations are found at 1822 cm^{-1} in the IR spectrum of free squaric acid [45]. This type of absorption is characteristic of salts of $C_nO_n^{2-}$ ion and it was found at 1500 cm^{-1} in the IR spectrum of $K_2C_4O_4$ [11]. The weak bands in the region of 400–500 and 500–600 cm^{-1} are due to M–N and M–O stretching vibrations, respectively.

Thermal analysis

The thermoanalytical curves of the complexes are shown in Figs 2–5.

The $[Co(tea)_2]sq\cdot 2H_2O$ complex exhibits three decomposition stages (Fig. 2). In the first stage, endothermic removal of two moles of crystal water molecule occurs in the temperature range of 65–104ºC (DTG_{max}= 85ºC). The complex melts at 196ºC and then in the temperature range of 168–342ºC, the anhydrous Co(II) complex involves the decomposition of neutral tea ligand by the endothermic effects (DTG_{max}=230, 309ºC). The following stage involves the burning of organic residue by the exothermic effect (DTG_{max}= 374ºC), leading finally to Co_3O_4. The endothermic peak at 898ºC (DTG_{max}) is related to the conversion of Co_3O_4 to CoO. The overall mass loss of 83.04% (calcd. 85.12%) agrees with the proposed structure well.

The $[Ni(tea)_2]sq$ complex has a high thermal stability (Fig. 3). Its decomposition begins at 225ºC after melting at 223ºC. In the temperature range of 225–353ºC, the first and second stages of the Ni(II) complex are related to the successive decomposition of the neutral tea ligands, by giving initially endothermic, and then an exothermic contribution is also observed in the DTA curve of the complex (DTG_{max}=289, 308ºC). The following stage involves the exothermic decomposition of squarate by released CO_2 and the extremely burning of organic residue, leading finally to NiO (found 83.32, calcd. 84.07%). This type of behaviour of oxalate complexes has been reported earlier [46].

Thermal decomposition of the $[Cu(tea)_2]sq$ complex proceeds in the three stages (Fig. 4). The complex is thermally stable up to about 162ºC and undergoes complete exothermic decompositions after melting at 154ºC. In the temperature range of 162–434ºC, the exothermic peaks (DTG_{max}=170, 278ºC) are related to the release of the tea ligands. In the third stage, the strong exothermic mass loss processes occurs in the temperature range of 434–542ºC. During this stage, the remaining organic part and squarate is abruptly burnt (DTG_{max}=ca. 500ºC). The final solid product of the thermal decomposition was identified as CuO (found 82.11, calcd. 83.22%).

The thermal behavior of the Cd(II) complex is different from the Co(II), Ni(II) and Cu(II) complexes (Fig. 5), because of the Cd(II) complex has different structure from the other complexes. The first stage

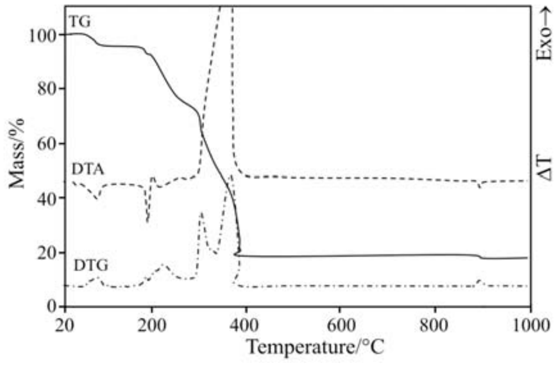

Fig. 2 TG, DTG and DTA curves of $[Co(tea)_2]sq\cdot 2H_2O$

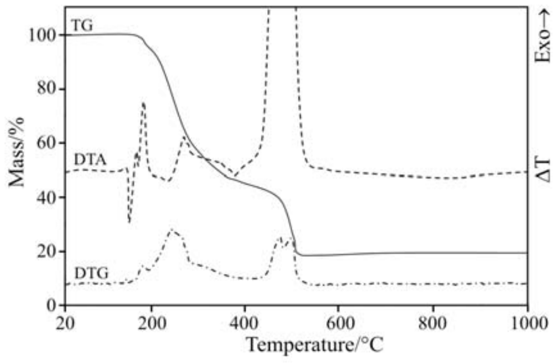

Fig. 4 TG, DTG and DTA curves of $[Cu(tea)_2]sq$

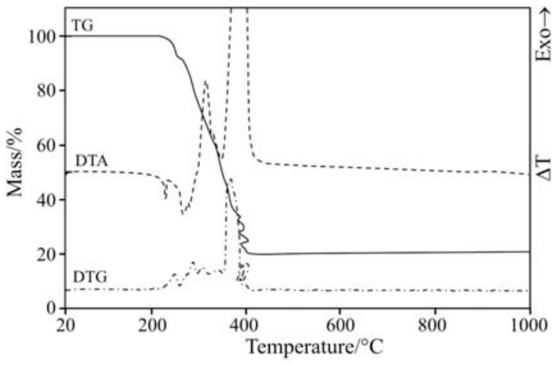

Fig. 3 TG, DTG and DTA curves of $[Ni(tea)_2]sq$

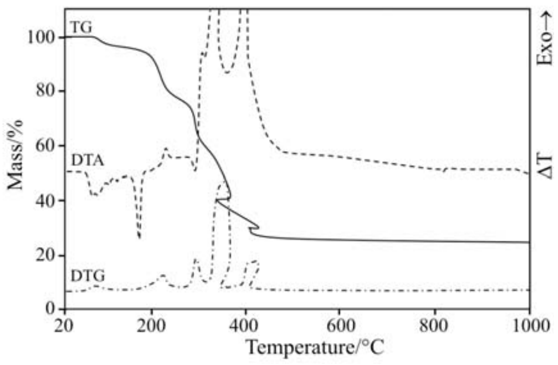

Fig. 5 TG, DTG and DTA curves of $[Cd(tea)_2]sq\cdot H_2O$ complex

(56–136ºC) is related to the dehydration of the complex. The anhydrous Cd(II) complex starts to decompose with melting at 184ºC (DTA). The second stage of $[Cd(tea)_2]sq$ is related to the decomposition of the neutral tea ligand in the temperature range of 184–314ºC (DTG_{max}=226ºC). The following exothermic stages between 315–470ºC (DTG_{max}=352 and 407ºC) are related to decomposition of the sq^{2-} and the extremely burning of organic residue. The final decomposition product is CdO (found 75.30, calcd. 76.35%).

The final decomposition products, namely CoO, NiO, CuO and CdO, were identified by IR spectroscopy. On the basis of the first DTG_{max} of the decompositions, the thermal stability of the anhydrous complexes follows the order: Ni(II), 251ºC>Cd(II), 226ºC> Co(II), 203ºC>Cu(II), 170ºC in static air atmosphere.

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