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THERMAL STUDIES OF COPPER(II) SQUARATE COMPLEXES OF DIAMINES IN THE SOLID STATE

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Abstract

$CuL_2C_4O_4$ [*L*=ethane-1,2-diamine (en)], $CuL_2C_4O_4{\cdot}2H_2O$ [*L*=N-methylethane-1,2-diamine (meen), N-ethylethane-1,2-diamine (eten), N-propylethane-1,2-diamine (pren), N-methyl-N'-ethylethane-1,2-diamine (meeten) and propane-1,2-diamine (pn)], $CuL_2C_4O_4{\cdot}0.5H_2O$ [*L*=N,N'-dimethylethane-1,2-diamine (dmeen)], $CuL_2C_4O_4{\cdot}4H_2O$ [*L*=propane-1,2-diamine (pn)] and $CuL_2C_4O_4{\cdot}H_2O$ [*L*=2-methylpropane-1,2-diamine (ibn)] have been synthesized by the addition of respective diamine to finely powdered $CuC_4O_4{\cdot}2H_2O$ and their thermal studies have been carried out in the solid state. $Cu(en)_2C_4O_4$ upon heating loses one molecule of diamine with sharp colour change yielding $Cu(en)C_4O_4$ which upon further heating transforms to unidentified products. All aquated-bis-diamine species [$CuL_2C_4O_4{\cdot}2H_2O$, $CuL_2C_4O_4{\cdot}0.5H_2O$ and $CuL_2C_4O_4{\cdot}H_2O$] upon heating undergo deaquation–anation reaction in the solid state showing thermochromism and transform to $CuL_2C_4O_4$, which revert on exposure to humid atmosphere (RH ~90%). All the squarato bis-diamine species, $CuL_2C_4O_4$, on further heating transform to unidentified products through the formation of $CuLC_4O_4$ as intermediates. The mono diamine species, have been isolated pyrolytically in the solid state and can be stored in a desiccator as well as in open atmosphere. They are proposed to be polymeric.

Keywords: copper(II) complexes, copper(II) squarate, TG-DTA, thermal decomposition

Introduction

Thermochromic phenomenon in diamine complexes of copper(II) is well documented in literature [1–7]. It is evident that the sudden colour change in these complexes is due to various reasons as follows: (i) a change in the in-plane ligand field strength caused by conformational changes in the diamine chelate rings; (ii) a change in the coordination geometry, and (iii) desolvation or deamination. From the reports available till date one may conclude that thermochromism largely depends on the nature of the diamine as well as the counter anions. Easily polarisable anions i.e. Br^-, I^-

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etc. generally exhibit continuous thermochromism [6, 8] whereas, less easily polarisable anions like ClO_4^-, BF_4^-, $CF_3CO_2^-$ show discontinuous thermochromism [2, 6]. In this context the study of amine complexes using squarate anion is relevant based on the following reasons: i) metal squarate does not decompose below 300°C [9], ii) squarate anion may exhibit versatile coordinating modes such as monodentate (squarato-O^1), bidentate squarate-O^1, O^2 and squarate-O^1, O^4) and/or bridging ligand [10–16] and iii) there is also the possibility of H-bonding network by the oxygen atoms of the squarate moiety with the amine hydrogen of diamines. Recently we reported thermal studies of amine complexes of nickel(II) and cadmium(II) with squarate as counter anion [17–19]. However, the thermal study of copper(II)-diamine complexes with squarate ($C_4O_4^{2-}$) as counter anion is not documented in literature. Here, we are reporting solid state thermal studies of copper(II) squarate complexes of diamines e.g.: (i) ethane-1,2-diamine (en) (ii) N-methylethane-1,2-diamine (meen), (iii) N-ethylethane-1,2-diamine (eten), (iv) N-propylethane-1,2-diamine (pren), (v) N,N'-dimethylethane-1,2-diamine (dmeen), (vi) N-methyl-N'-ethylethane-1,2-diamine (meeten), (vii) propane-1,2-diamine (pn) and (viii) 2-methylpropane-1,2-diamine (ibn).

Experimental

High purity 3,4-dihydroxy-3-cyclobutene-1,2-dione (squaric acid), en, meen, eten, pren, dmeen, meeten, pn and ibn were purchased from Aldrich Chemical Company Inc. and used as received. All other chemicals were of AR grade. Copper(II) squarate dihydrate, was prepared according to the literature reported [15]. Elemental analyses (carbon, hydrogen and nitrogen) were performed using a Perkin Elmer 240C elemental analyzer and copper(II) content was estimated iodometrically [20]. IR-spectra (4000–400 cm^{-1}) and electronic spectra were taken using Nicolet FT-IR 755 (where KBr was used as medium material) and Shimadzu UV 2100 spectrophotometer respectively. The magnetic susceptibility was measured at 27°C using an EG and G PAR 155 vibrating sample magnetometer, where $Hg[Co(SCN)_4]$ was used as a reference material and diamagnetic corrections were made using Pascal's constants [21]. Thermal analysis (TG-DTA) was carried out using Shimadzu DT-30 thermal analyzer in a dynamic atmosphere of nitrogen (flow rate: 30 mL min^{-1}). The sample (particle size of 150–200 mesh) was heated in a platinum crucible at a rate 10°C min^{-1} with inert alumina as reference material.

Preparation of the complexes

The diamine complexes of copper(II) squarate were prepared by using the following techniques.

Technique 1

Diamine (3–4 mmol) was added to finely powdered copper(II) squarate (1 mmol) and the resulting mixture was kept in a stoppered conical flask. After a few days the mix-

Table 1 Elemental analyses, magnetic and electronic (Nujol) spectral data for diamine complexes of copper(II) squarate

Complex	No.	Colour	Elemental analyses/%*				μ_{eff}/B.M.	λ_{max}/nm
			Cu	C	H	N		
$Cu(en)_2C_4O_4$	**1**	bluish violet	21.48 (21.49)	32.46 (32.48)	5.44 (5.41)	18.92 (18.94)	1.79	557
$Cu(en)C_4O_4$	**1a**	brown	26.98 (26.97)	30.55 (30.56)	3.40 (3.39)	11.88 (11.88)	1.54	581
$Cu(meen)_2C_4O_4\cdot 2H_2O$	**2**	violet	17.64 (17.67)	33.38 (33.37)	6.68 (6.67)	15.59 (15.57)	1.75	540
$Cu(meen)C_4O_4$	**2a**	greenish brown	25.42 (25.46)	33.69 (33.66)	3.89 (4.00)	11.00 (11.22)	1.47	585
$Cu(eten)_2C_4O_4\cdot 2H_2O$	**3**	violet	16.41 (16.39)	37.10 (37.15)	7.21 (7.22)	14.47 (14.45)	1.70	536
$Cu(eten)C_4O_4$	**3a**	light brown	24.14 (24.11)	36.40 (36.42)	4.57 (4.55)	10.60 (10.62)	1.51	578
$Cu(pren)_2C_4O_4\cdot 2H_2O$	**4**	blue	15.31 (15.29)	40.41 (40.42)	7.71 (7.70)	13.47 (13.47)	1.77	586
$Cu(pren)C_4O_4$	**4a**	brown	22.84 (22.89)	39.00 (38.91)	5.01 (5.04)	10.04 (10.08)	1.48	584
$Cu(dmeen)_2C_4O_4\cdot 0.5H_2O$	**5**	light blue	17.60 (17.62)	39.95 (39.94)	6.92 (6.93)	15.52 (15.53)	1.79	578
$Cu(dmeen)C_4O_4$	**5a**	brown	24.08 (24.10)	36.41 (36.42)	4.56 (4.55)	10.64 (10.62)	1.51	586

Table 1 Continued

Complex	No.	Colour	Elemental analyses/%*				μ_{eff}/B.M.	λ_{max}/nm
			Cu	C	H	N		
$Cu(meeten)_2C_4O_4{\cdot}2H_2O$	**6**	deep blue	15.30 (15.29)	40.43 (40.42)	7.71 (7.70)	13.48 (13.47)	1.77	592
$Cu(meeten)C_4O_4$	**6a**	brown	22.91 (22.89)	38.94 (38.91)	5.02 (5.04)	10.04 (10.08)	1.59	588
$Cu(pn)_2C_4O_4{\cdot}2H_2O$	**7**	violet	17.69 (17.67)	33.36 (33.37)	6.69 (6.67)	15.58 (15.57)	1.73	541
$Cu(pn)C_4O_4$	**7a**	light brown	25.30 (25.46)	33.81 (33.66)	4.20 (4.00)	11.19 (11.22)	1.50	580
$Cu(pn)_2C_4O_4{\cdot}4H_2O^*$	**8**	deep violet	16.41 (16.39)	31.00 (30.96)	7.19 (7.22)	14.47 (14.45)	1.74	538
$Cu(pn)C_4O_4$	**8a**	light brown	25.35 (25.46)	33.78 (33.66)	4.18 (4.00)	11.20 (11.22)	1.48	578
$Cu(ibn)_2C_4O_4{\cdot}H_2O$	**9**	deep blue	17.20 (17.19)	38.95 (38.96)	7.00 (7.03)	15.16 (15.15)	1.78	541
$Cu(ibn)C_4O_4$	**9a**	brown	24.07 (24.10)	36.40 (36.42)	4.58 (4.55)	10.60 (10.62)	1.48	576

*The complex is obtained by following technique 2 ture was treated with ethanol to wash out the excess ligand. Then the resulting mixture was treated with water and filtered. Upon keeping the filtrate in a $CaCl_2$ desiccator the desired complex was separated out and then filtered, washed with isopropanol and dried over a $CaCl_2$ desiccator.

Technique 2

Copper(II) squarate dihydrate (1 mmol) was dissolved in minimum amount of aqueous ammonia (25%), (5 cm^3), to which diamine (3–4 mmol) was added. The resulting mixture was heated on a water bath in order to remove any ammonia, and then isopropanol (10 cm^3) was added. The complex, which separated out, was filtered, washed with isopropanol and dried over a $CaCl_2$-desiccator.

The composition of the complexes along with elemental analyses, electronic spectral and magnetic data are shown in Table 1.

Results and discussion

We have recrystallised the complexes several times and the purity is assured from reproducible elemental analyses, IR and electronic spectra, magnetic and thermal analyses (TG-DTA). In case of nickel(II) squarate complexes of diamine and its derivatives we were successful to synthesise conformational isomers on varying the synthetic procedures. But in case of cadmium(II) squarate–diamine system we did not get such type of isomers. Here we have got always identical species on changing the synthetic routes except for propane-1, 2-diamine ligand where complexes with two different compositions were obtained on changing the synthetic procedures (*vide* Experimental). Elemental analyses reveal that five types of complexes i.e., (i) $Cu(en)_2C_4O_4$ **1,** (ii) $CuL_2C_4O_4.2H_2O$ (*L*=meen **2**, eten **3**, pren **4**, meeten **6** and pn **7**), (iii) $Cu(dmeen)_2C_4O_4{\cdot}0.5H_2O$ **5,** (iv) $Cu(pn)_2C_4O_4.4H_2O$ **8** and (v) $Cu(ibn)_2(C_4O_4){\cdot}H_2O$ **9** are obtained. IR bands due to $\nu(NH_2)$ and $\nu(CH_2)$ exhibited by all the complexes are comparable to those of similar diamine systems whose chelate character has been established by X-ray single crystal analysis [7–8]. In order to determine whether the squarate anion is coordinated or acting as counter anion in complex species we have examined IR spectra (Table 2) of the complexes in the region of 1400–1800 cm^{-1} where the characteristic bands for different modes of coordination of $C_4O_4^{2-}$ are observed [15]. All the complexes, except $Cu(en)_2C_4O_4$, exhibit a very strong and broad band in the region of 1440–1550 cm^{-1} and only one sharp band at ~1720 cm^{-1} (Table 2). The former band is assigned to a mixture of ν(C–C) and ν(C–O) stretching vibration and the latter one is due to ν(C=O) of a squarate ligand and thus suggesting that $C_4O_4^{2-}$ ion acts as a counter anion rather than a coordinated ligand in all cases [17–19]. In case of $Cu(en)_2C_4O_4$ the IR bands assigned to ν(C–C) and ν(C–O) stretching vibration of the squarate moiety shift towards a lower wave number region with splitting (~1477 and ~1435 cm^{-1}, Table 2), the band corresponds to ν(C=O) becomes weakened and one additional band ~1610 cm^{-1} assigned to ν(C=C) is obtained indicating the linkage of squarate ligand with Cu(II) centre [17–19]. All the aquated species show IR band at ~700 cm^{-1} corresponds to $\rho_w(H_2O)$ suggesting coordination of water molecule in them. All the complexes exhibit magnetic susceptibility of ~1.75 B.M. at 25°C as is expected for mononuclear Cu(II) system. The electronic spectral band positions (only *d–d* transition) of the complexes are presented in Table 1. The routine physico-chemical studies as discussed above are not enough to predict the exact structures of Cu(II) complexes and for this X-ray single crystal structural analysis is needed. But all our attempts to prepare single crystals of the complexes have failed. Therefore, we are not ascertained about the structures of the complexes though the most probable structure of the complexes discussed above should be octahedral.

Thermal studies

$Cu(en)_2C_4O_4$ **1** upon heating loses one molecule of diamine in single step as is evident from TG-DTA curves (Scheme 1; Fig. 1) and transforms to $Cu(en)C_4O_4$ **1a** showing thermochromism, blue violet→brown. The complexes $CuL_2C_4O_4{\cdot}2H_2O$ (*L*=meen **2**, eten **3**, pren **4**, meeten **6** and pn **7**), upon heating lose two molecules of water with colour changes, violet→blue for (meen) and (pn), violet→green for (eten), blue→light green for (pren), deep blue→light green for (meeten) yielding $CuL_2C_4O_4$ (Scheme 1; Figs 1 and 2). The light blue, $Cu(dmeen)_2C_4O_4{\cdot}0.5H_2O$ **5** and deep blue, $Cu(ibn)_2(C_4O_4){\cdot}H_2O$ **9** complexes also upon heating undergo deaquation generating $Cu(dmeen)_2C_4O_4$ (green) and $Cu(ibn)_2C_4O_4$ (violet) respectively (Scheme 1; Fig. 2). The complex $Cu(pn)_2(C_4O_4){\cdot}4H_2O$, **8** which is obtained by adopting technique 2, upon heating loses all four water

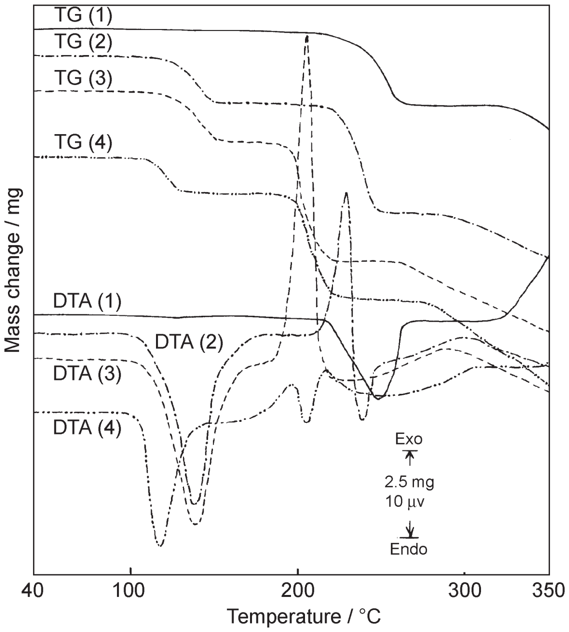

Fig. 1 TG-DTA curves: $Cu(en)_2C_4O_4$ (**1**) (mass taken=8.56 mg) (—), $Cu(meen)_2C_4O_4{\cdot}2H_2O$ (**2**) (mass taken=11.67 mg) (···), $Cu(eten)_2C_4O_4{\cdot}2H_2O$ (**3**) (mass taken=15.01 mg) (---) and $Cu(pren)_2C_4O_4{\cdot}2H_2O$ (**4**) (mass taken=12.05 mg) (····)

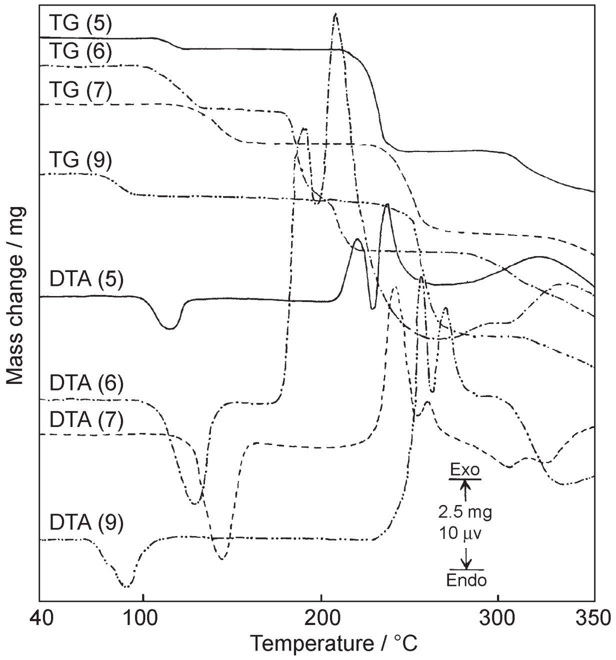

Fig. 2 TG-DTA curves: Cu(dmeen)$_2$C$_4$O$_4$·0.5H$_2$O (**5**) (mass taken=11.00 mg) (—), Cu(meeten)$_2$C$_4$O$_4$·2H$_2$O (**6**) (mass taken=13.93 mg) (···), Cu(pn)$_2$C$_4$O$_4$·2H$_2$O (**7**) (mass taken=10.13 mg) (---) and Cu(ibn)$_2$C$_4$O$_4$·H$_2$O (**9**) (mass taken= 13.99 mg) (···)

molecules in a single step to produce Cu(pn)$_2$(C$_4$O$_4$). The IR spectra (1440–1550 cm^{-1}) of all the dehydrated bis-diamine species are similar to Cu(en)$_2$C$_4$O$_4$ (Table 2) suggesting squarate anation in them. The species CuL$_2$C$_4$O$_4$ revert on keeping them in humid (RH ~90%) atmosphere for 20–24 h. Deaquation reaction in all cases, except for the (ibn) complex, takes places at >100°C, suggesting that the water molecules are coordinated whereas, in case of Cu(ibn)$_2$(C$_4$O$_4$)·H$_2$O **9** deaquation starts at ~70°C (Scheme 1; Fig. 2). This is probably due to steric effect exerted by two methyl groups present in one of the carbons of the diamine chain, which makes the coordinated water molecules labile. On the other hand, it is interesting to note that the complex, Cu(pn)$_2$(C$_4$O$_4$)·4H$_2$O **8** starts deaquation at ~100°C although all the water molecules are not coordinated suggesting crystal waters are in hydrogen bonding network. All the deaquated bis(diamine), CuL$_2$C$_4$O$_4$ upon further heating lose one molecule of diamine and transform to CuLC$_4$O$_4$ before decomposition to unidentified products (Scheme 1). The monodaimine species can be isolated pyrolytically in the solid state and can be stored in a desiccator as well as in open atmosphere. The deamination reaction is also followed by prominent colour changes (Scheme 1). On the basis of initial temperature of deamination (T_i) thermal stability of the bis(diamine) species has been observed and order of stability is as follows: ibn>pn>en>meen~dmen>eten>pren>meeten (Scheme 1). This order reveals that the

$$\mathrm{Cu(en)_2C_4O_4}\ (\mathbf{1}) \xrightarrow{210-265^\circ\mathrm{C}} \mathrm{Cu(en)C_4O_4}\ (\mathbf{1a}) \xrightarrow{\approx 320^\circ\mathrm{C}} \mathrm{X} \tag{i}$$

$$\begin{gathered}\mathrm{Cu(meen)_2C_4O_4{\cdot}2H_2O}\ (\mathbf{2}) \xleftrightarrow[\mathrm{H}]{110-140^\circ\mathrm{C}} \mathrm{Cu(meen)_2C_4O_4} \\ \xrightarrow{205-250^\circ\mathrm{C}} \mathrm{Cu(meen)C_4O_4} \xrightarrow{\approx 285^\circ\mathrm{C}} \mathrm{X}\ \ (\mathbf{2a})\end{gathered} \tag{ii}$$

$$\begin{gathered}\mathrm{Cu(eten)_2C_4O_4{\cdot}2H_2O}\ (\mathbf{3}) \xleftrightarrow[\mathrm{H}]{105-150^\circ\mathrm{C}} \mathrm{Cu(eten)_2C_4O_4} \\ \xrightarrow{190-215^\circ\mathrm{C}} \mathrm{Cu(eten)C_4O_4} \xrightarrow{\approx 265^\circ\mathrm{C}} \mathrm{X}\ \ (\mathbf{3a})\end{gathered} \tag{iii}$$

$$\begin{gathered}\mathrm{Cu(pren)_2C_4O_4{\cdot}2H_2O}\ (\mathbf{4}) \xleftrightarrow[\mathrm{H}]{105-120^\circ\mathrm{C}} \mathrm{Cu(pren)_2C_4O_4} \\ \xrightarrow{185-235^\circ\mathrm{C}} \mathrm{Cu(pren)C_4O_4} \xrightarrow{\approx 270^\circ\mathrm{C}} \mathrm{X}\ \ (\mathbf{4a})\end{gathered} \tag{iv}$$

$$\begin{gathered}\mathrm{Cu(dmeen)_2C_4O_4{\cdot}0.5H_2O}\ (\mathbf{5}) \xleftrightarrow[\mathrm{H}]{105-120^\circ\mathrm{C}} \mathrm{Cu(dmeen)_2C_4O_4} \\ \xrightarrow{205-245^\circ\mathrm{C}} \mathrm{Cu(dmeen)C_4O_4}\ (\mathbf{5a}) \xrightarrow{\approx 305^\circ\mathrm{C}} \mathrm{X}\end{gathered} \tag{v}$$

$$\begin{gathered}\mathrm{Cu(meeten)_2C_4O_4{\cdot}2H_2O}\ (\mathbf{6}) \xleftrightarrow[\mathrm{H}]{95-125^\circ\mathrm{C}} \mathrm{Cu(meeten)_2C_4O_4} \xrightarrow{175-220^\circ\mathrm{C}} \\ \mathrm{Cu(meeten)C_4O_4}\ (\mathbf{6a}) \xrightarrow{\approx 290^\circ\mathrm{C}} \mathrm{X}\end{gathered} \tag{vi}$$

$$\begin{gathered}\mathrm{Cu(pn)_2C_4O_4{\cdot}2H_2O}\ (\mathbf{7}) \xleftrightarrow[\mathrm{H}]{115-160^\circ\mathrm{C}} \mathrm{Cu(pn)_2C_4O_4} \xrightarrow{215-270^\circ\mathrm{C}} \\ \mathrm{Cu(pn)C_4O_4}\ (\mathbf{7a}) \xrightarrow{\approx 280^\circ\mathrm{C}} \mathrm{X}\end{gathered} \tag{vii}$$

$$\begin{gathered}\mathrm{Cu(pn)_2C_4O_4{\cdot}4H_2O}\ (\mathbf{8}) \xleftrightarrow[\mathrm{H}]{100-165^\circ\mathrm{C}} \mathrm{Cu(pn)_2C_4O_4} \xrightarrow{220-265^\circ\mathrm{C}} \\ \mathrm{Cu(pn)C_4O_4}\ (\mathbf{8a}) \xrightarrow{\approx 280^\circ\mathrm{C}} \mathrm{X}\end{gathered} \tag{viii}$$

$$\begin{gathered}\mathrm{Cu(ibn)_2C_4O_4{\cdot}H_2O}\ (\mathbf{9}) \xleftrightarrow[\mathrm{H}]{70-95^\circ\mathrm{C}} \mathrm{Cu(ibn)_2C_4O_4} \xrightarrow{220-285^\circ\mathrm{C}} \\ \mathrm{Cu(ibn)C_4O_4}\ (\mathbf{9a}) \xrightarrow{\approx 310^\circ\mathrm{C}} \mathrm{X}\end{gathered} \tag{ix}$$

X=unidentified product, and H=humid atmosphere (R.H.> 60%)

Scheme 1

complexes of C-substituted diamines (ibn and pn) are thermally more stable than those of ethane-1,2-diamine and its N-substituted derivatives, the stability of which decreases with increasing the size of the alkyl group. IR spectral studies of $CuLC_4O_4$ show that shifting of the characteristics IR bands of the squarate moiety to a lower energy region (1430–1500 cm^{-1}) has taken place suggesting squarate ligand coordination in them [19]. But it is very difficult to comment on the mode of coordination of the squarate moiety based on IR spectroscopy. However, $CuLC_4O_4$ species exhibit relatively low magnetic susceptibility value in comparison to mononuclear copper(II) system at room temperature (Table 1) indicating antiferromagnetic interaction in them which may be explained by considering super exchange mechanism as it is observed in oxalato/acetato bridged polynuclear Cu(II)- system. The foregoing facts hint that the squarato moiety is involved in bridging in mono-diamine Cu(II) species. Here, it is to note that our all attempts to synthesize single crystals of the mono-species have failed and, therefore, we are unable to put forward the exact structure as well as the magneto-structural correlation of mono-(diamine) species.

Table 2 IR-bands of the complexes attributable to the squarate ligand in the 1850–1400 (cm^{-1}) region

Compound	ν(C=O)	ν(C=C)	ν[(C–C)+(C–O)]
$Cu(en)_2C_4O_4$	1705 w	1610 m	1477 vs, br, 1435 w
$Cu(en)C_4O_4$	1712 w	1611 m	1460 vs, br
$Cu(meen)_2C_4O_4{\cdot}2H_2O$	1710 s	a	1540 vs, br 1465 w
$Cu(meen)C_4O_4$	1723 w	1600 m	1487 vs, br 1433 w
$Cu(eten)_2C_4O_4{\cdot}2H_2O$	1705 s	a	1535 vs, br 1440 w
$Cu(eten)C_4O_4$	1728 w	1617 m	1493 vs, br
$Cu(pren)_2C_4O_4{\cdot}2H_2O$	1702 s	a	1545 vs, br1442w
$Cu(pren)C_4O_4$	1731 w	1608 m	1481 vs, br 1439 w
$Cu(dmeen)_2C_4O_4{\cdot}0.5H_2O$	1705 s	a	1525 vs,br, 1450 w
$Cu(dmeen)C_4O_4$	1735 w	1611 m	1483 vs, br 1440 w
$Cu(meeten)_2C_4O_4{\cdot}2H_2O$	1705 s	a	1540 vs, br, 1445 w
$Cu(meeten)C_4O_4$	1702 w	1610 m	1478 vs, br, 1429 w
$Cu(pn)_2C_4O_4{\cdot}2H_2O$	1705 s	a	1533 vs,br, 1443 w
$Cu(pn)C_4O_4$	1738 w	1614 m	1488 vs, br, 1438 w
$Cu(ibn)_2C_4O_4{\cdot}H_2O$	1710 s	a	1539 vs, br, 1442 w
$Cu(ibn)C_4O_4$	1715 w	1620 m	1478 vs, br, 1449 w

s=strong, vs=very strong, w=weak, m=medium, br=broad

a) Here $C_4O_4^{2-}$ anion does not take part in coordination. As a result, C=C becomes too weak to exhibit IR band at ca 1600 cm^{-1}

Diamine complexes of copper(II) squarate also exhibit discontinuous thermochromism. All the monodiamine species are brown in colour but their parent species have different colours and pyrolytic method is the only way to synthesise them.

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