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PREPARATION, CHARACTERIZATION AND SOLID STATE THERMAL STUDIES OF CADMIUM(II) SQUARATE COMPLEXES OF ETHANE-1,2-DIAMINE AND ITS DERIVATIVES

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Abstract

$[CdL_3]C_4O_4$ [*L*=ethane-1,2-diamine (en)], $[CdL_2(H_2O)_2]C_4O_4$ [*L*=N-methylethane-1,2-diamine (meen), N-ethylethane-1,2-diamine (eten), N-propylethane-1,2-diamine (pren), propane-1,2-diamine (pn) and N-methylpropane-1,2-diamine (ibn)] and $[CdL_2(C_4O_4)]$ [*L*=N-isopropylethane-1,2-diamine (ipren)] have been synthesized by the addition of the respective diamine to finely powdered $CdC_4O_4{\cdot}2H_2O$ and their thermal studies have been carried out in the solid state. $[Cd(en)_3]C_4O_4$ upon heating loses two molecules of diamine in two overlapping steps yielding $Cd(en)C_4O_4$ which upon further heating transforms to unidentified products. The diaquabis(diamine) species, $[CdL_2(H_2O)_2]C_4O_4$, show thermally induced deaquation-anation reaction in the solid state and thereby produce $[CdL_2(C_4O_4)]$, which reverts on exposure to humid atmosphere (*RH*=90%) for 20–24 h. All the squarato bis(diamine) species, $[CdL_2(C_4O_4)]$, on pyrolysis in the solid state transform to unidentified products through the formation of intermediates, $CdL_{1.5}C_4O_4$, (*L*=meen, pren and ipren), $CdLC_4O_4$ (*L*=meen, eten, pren, ipren, pn and ibn) and $CdL_{0.5}C_4O_4$ (*L*=eten, pn and ibn). However, amongst the intermediates only the mono diamine species, $CdLC_4O_4$ can be isolated in pure form and the pyrolytic process is the only way to synthesize them. The monodiamine species can be stored in a desiccator as well as in an open atmosphere and proposed to have a polymeric structure.

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

Introduction

Solid state thermal studies of M(II) complexes [*M*=Ni(II), Cu(II), Zn(II) and Cd(II)] of ethane-1,2-diamine and their derivatives are well documented [1–4]. It is observed that the thermal properties of the complexes are mainly influenced by the steric and inductive effect of the substituent group of the diamine moiety and the nature of the counter anion. The anions like NO_3^-, NO_2^-, SCN^- etc. having various modes of coordination are prone to exhibit thermally induced configurational isomerism [1(b)],

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whereas, anions like Cl^-, Br^-, I^-, BF_4^-, SO_4^{2-}, SeO_4^{2-}, $CCl_3CO_2^-$, $CBr_3CO_2^-$, $CF_3CO_2^-$, etc. are susceptible to show thermally induced conformational isomerism [1(*d*)] as a result of changing the H-bonding network between amine hydrogen and the electronegative atom of the anions on thermal excitation. Here it is interesting to note that the diamine complexes having anions like $CBr_3CO_2^-$, $CCl_3CO_2^-$, $CF_3CO_2^-$, etc. can not produce diamine deficient complexes upon heating as the corresponding salts usually undergo decomposition before diamine elimination, whereas, with anions like Cl^-, SO_4^{2-}, SeO_4^{2-} etc. the diamine deficient complexes are documented due to the high thermal stability of the corresponding salts. In this context the study of amine complexes using squarate ($C_4O_4^{2-}$) anion is relevant due the following reasons: (i) solid state thermal studies of several metal squarates reveal that the squarate moiety does not usually undergo decomposition below 300°C [5], (ii) the squarate ($C_4O_4^{2-}$) anion may exhibit versatile coordinating modes such as monodentate (squarato-O^1), bidentate (squarato-O^1, O^2 and squarato-O^1, O^4) and/or bridging ligand [6–12] and (iii) there is a possibility of exhibiting H-bonding network by the oxygen atoms of $C_4O_4^{2-}$ unit with the amine hydrogen of diamines.

Insolubility of metal squarates in common solvents makes the synthesis of its amine complexes difficult. However, we overcame this problem efficiently and reported recently the synthesis, characterization and solid state thermal studies of diamine and triamine complexes of nickel(II) squarate [13, 14]. Preparation of isomeric complexes by changing the synthetic techniques, studies of thermally induced phase transition and syntheses of amine deficient complexes were the noteworthy features of those studies. We are reporting herein the synthesis, characterization and solid state thermal studies of cadmium(II) squarate complexes with seven 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-isopropylethane-1,2-diamine (ipren), (vi) propane-1,2-diamine (pn) and (vii) N-methylpropane-1,2-diamine (ibn).

Experimental

High purity 3,4-dihydroxy-3-cyclobutene-1,2-dione (squaric acid), en, meen, eten, pren, ipren, pn and ibn were purchased from Aldrich Chemical Company Inc. and used as received. All other chemicals were of AR grade. Cadmium(II) squarate dihydrate, was prepared by the reaction of squaric acid with cadmium(II) acetate dihydrate [15]. 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. Elemental analyses were performed using a Perkin Elmer 240°C elemental analyzer. IR-spectra (4000–400 cm^{-1}) were taken at 27°C using a Nicolet FT-IR 755 where KBr was used as medium material.

Preparation of the complexes

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

Technique 1

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

Cadmium(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.

Table 1 Elemental analyses of diamine complexes of cadmium(II) squarate

Complex	No.	Analyses/%			
		Cd	C	H	N
$[Cd(en)_3]C_4O_4$	1	27.7(27.8)	29.4(29.6)	5.3(5.9)	20.4(20.7)
$Cd(en)(C_4O_4)$	1a	40.0(39.5)	25.5(25.3)	2.8(2.8)	10.2(9.8)
$[Cd(meen)_2(H_2O)_2]C_4O_4$	2	27.8(27.4)	29.3(29.3)	5.6(5.8)	13.8(13.7)
$Cd(meen)(C_4O_4)$	2a	38.2(37.6)	27.8(28.1)	3.26(3.3)	10.6(9.3)
$[Cd(eten)_2(H_2O)_2]C_4O_4$	3	25.7(25.5)	32.9(33.0)	6.4(6.3)	12.8(12.7)
$Cd(eten)(C_4O_4)$	3a	36.9(35.9)	31.2(30.7)	4.3(3.8)	9.7(8.9)
$[Cd(pren)_2(H_2O)_2]C_4O_4$	4	24.2(24.4)	36.1(35.9)	6.8(6.8)	12.0(12.2)
$Cd(pren)(C_4O_4)$	4a	35.6(34.4)	33.9(33.0)	3.7(4.2)	9.2(8.5)
$[Cd(ipren)_2(C_4O_4)]$	5	26.2(26.4)	39.2(39.3)	6.5(6.4)	13.0(13.2)
$Cd(ipren)(C_4O_4)$	5a	36.0(34.4)	34.4(33.0)	5.0(4.2)	9.1(8.5)
$[Cd(pn)_2(H_2O)_2]C_4O_4$	6	27.5(27.6)	29.3(29.5)	5.8(6.0)	13.7(13.7)
$Cd(pn)(C_4O_4)$	6a	39.0(37.6)	29.0(28.1)	3.7(3.3)	10.5(9.3)
$[Cd(ibn)_2(H_2O)_2]C_4O_4$	7	25.7(25.8)	32.9(33.1)	6.4(6.3)	12.8(12.6)
$Cd(ibn)(C_4O_4)$	7a	34.2(35.9)	31.3(30.7)	4.1(3.8)	9.9(8.9)

[a] Percentage in parentheses are theoretically calculated values

Results and discussion

The complexes are recrystallized several times and the purity is assured from their reproducible elemental analyses, IR-spectral and thermal (TG-DTA) data. Earlier, we observed variation in composition while synthesizing diamine complexes of $NiC_4O_4{\cdot}2H_2O$ altering the preparative procedure, but here with $CdC_4O_4{\cdot}2H_2O$ we do not find any such variation in composition. Elemental analyses (Table 1) reveal that only ethane-1,2-diamine (en) produces tris-species, $[Cd(en)_3]C_4O_4$, whereas, all other substituted diamines yield bis-species $[CdL_2(H_2O)_2]C_4O_4$ (*L*=meen, eten, pren, pn, and ibn) and $[CdL_2C_4O_4]$ (*L*=ipren). It is to note that the substituted diamines do not produce any tris-species probably due to the steric effect of the substituted groups.

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 have been established by X-ray single crystal analyses [1(*d*)]. In order to determine whether the squarate ion is coordinated or acting as a counter anion in a complex species we have examined the IR-spectra (Table 2; Fig. 1) of the complexes in the region of 1400–1800 cm^{-1}, where the characteristic bands for different modes of coordination of $C_4O_4^{2-}$ ion are

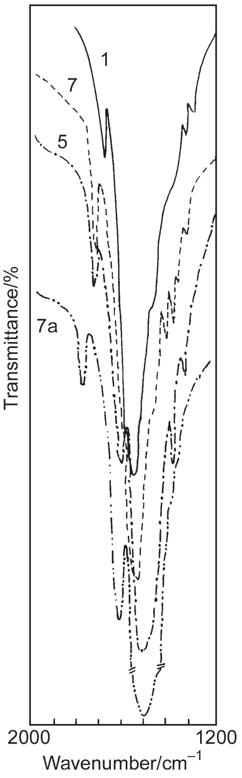

Fig. 1 IR-spectra (KBr) of $[Cd(en)_3]C_4O_4$ (**1**) (—), $[Cd(ibn)_2(H_2O)_2]C_4O_4$ (**7**) (- - -), $[Cd(ipren)_2(C_4O_4)]$ (**5**) (-·-·-) and $Cd(ibn)(C_4O_4)$ (**7a**) (-··-··-)

observed. $[Cd(en)_3]C_4O_4$ exhibits a very strong and broad band in the region of 1440–1550 and only one sharp band at 1702 cm^{-1}. 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 thereby suggesting that $C_4O_4^{2-}$ ion is acting as counter anion rather than a coordinated ligand. The above facts suggest octahedral geometry having N_6-chromophore around Cd(II) in complex **1**.

The complexes, $[CdL_2(H_2O)_2]C_4O_4$ (*L*=meen, eten, pren, pn and ibn) show very similar IR bands as those exhibited by complex **1** in the region of 1440–1550 cm^{-1} (strong and broad, Fig. 1) and one sharp band at ca 1710 cm^{-1} (Fig. 1) indicating that $C_4O_4^{2-}$ is also acting as counter anion in them. The IR-band at 700 cm^{-1} corresponds to $\rho w(H_2O)$ exhibited by all the above complexes suggests the coordination of the water molecules in them. Thereby, they also possess octahedral geometry with N_4O_2-chromophore around Cd(II). In complex, $[CdL_2C_4O_4]$, (*L*=ipren) 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 (~1538 cm^{-1} vs, br) and the high energy band assigned to νC=O (~1710 cm^{-1}), (observed in tris(diamine) and diaquabis(diamine) species) becomes

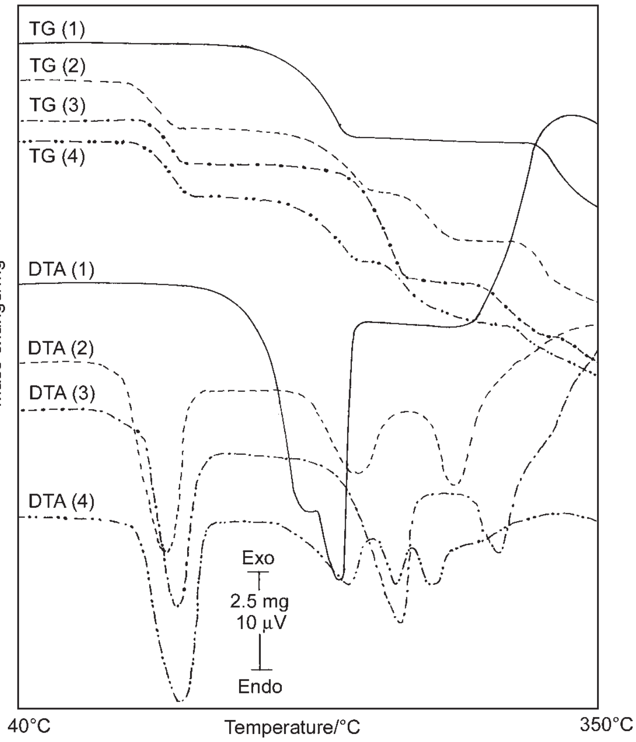

Fig. 2 TG-DTA curves for $[Cd(en)_3]C_4O_4$ (**1**) (mass taken=8.75 mg) (—) $[Cd(meen)_2(H_2O)_2]C_4O_4$ (**2**) (mass taken=15.12 mg) (- - -), $[Cd(eten)_2(H_2O)_2]C_4O_4$ (**3**) (mass taken=14.76 mg) (-·-·-) and $[Cd(pren)_2(H_2O)_2](C_4O_4)$ (**4**) (mass taken=16.02 mg) (-··-··)

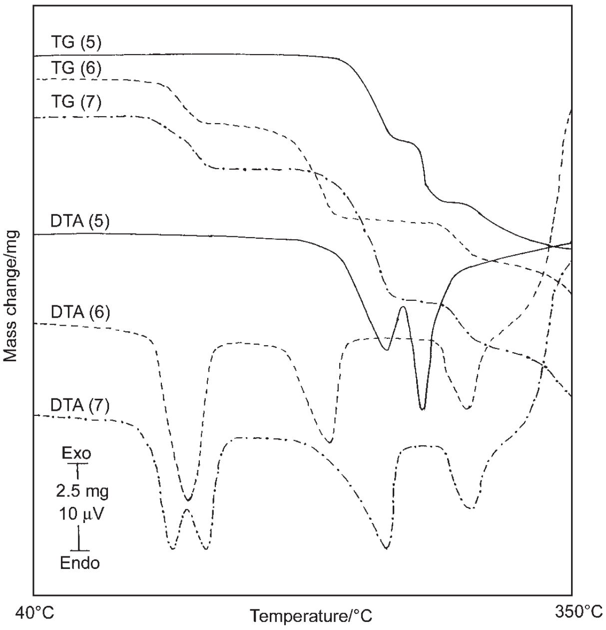

Fig. 3 TG-DTA curves for [Cd(ipren)$_2$C$_4$O$_4$] (**5**) (mass taken=18.11 mg) (—) [Cd(pn)$_2$(H$_2$O)$_2$]C$_4$O$_4$ (**6**) (mass taken=15.19 mg) (- - -) and [Cd(ibn)$_2$(H$_2$O)$_2$]C$_4$O$_4$ (**7**) (mass taken=18.68 mg) (-·-·-)

weakend and one additional band appears at 1620 cm^{-1}, ν(C=C), suggesting squarate ion linkage to cadmium(II). Here, it is to note that from the IR-spectral study it is not possible to identify the exact mode of coordination of the squarate ion. So it is very difficult to predict the most probable structure of it without X-ray single crystal structure determination. Unfortunately it does not produce suitable single crystals in spite of repeated attempts. However, it will not be irrational to consider that it may be either a polymeric species bridging through squarate or mononuclear penta (squarate-O^1)/hexa (squarate-O^{1,2}) coordinated.

[Cd(en)$_3$]C$_4$O$_4$ (**1**) upon heating loses two molecule of diamine in two overlapping steps yielding Cd(en)C$_4$O$_4$ as is evident from TG-DTA curves (Scheme 1; Fig. 2). The species, [Cd(ibn)$_2$(H$_2$O)$_2$]C$_4$O$_4$, upon heating undergoes deaquation-anation reaction in two steps whereas, all other diaquabis(diamine) species lose water molecule in single step yielding CdL$_2$C$_4$O$_4$, (Figs 2 and 3) which revert on keeping them in an open atmosphere for 20–24 h (Scheme 1). The IR-spectra (1440–1550 cm^{-1}) of the dehydrated complexes are similar to that of [Cd(ipren)$_2$C$_4$O$_4$] suggesting squarate anation in them (vide supra). Amongst the squarate bis(diamine) complexes, CdL$_2$C$_4$O$_4$, (*L*=eten, pn and ibn) upon further heating undergo decomposition with the formation of CdLC$_4$O$_4$ and CdL$_{0.5}$C$_4$O$_4$ as intermediates evident from their plateaus observed in the respective TG-curves (Figs 2 and 3; Scheme 1), whereas, $CdL_2C_4O_4$, (L=meen, pren and ipren) decompose through the formation of intermediates, $CdL_{1.5}C_4O_4$ and $CdLC_4O_4$ (Figs 2 and 3; Scheme 1).

$$\text{(i)}\quad [Cd(en)_3]C_4O_4\ (1) \xrightarrow[H]{155\text{–}225^\circ C} Cd(en)(C_4O_4)\ (1a) \xrightarrow{\sim 325^\circ C} X$$

$$\text{(ii)}\quad \begin{array}{l} [Cd(meen)_2(H_2O)_2]C_4O_4\ (2) \xleftrightarrow[H]{85\text{–}110^\circ C} Cd(meen)_2(C_4O_4) \xrightarrow{185\text{–}220^\circ C} \\ Cd(meen)_{1.5}(C_4O_4) \xrightarrow{240\text{–}265^\circ C} Cd(meen)(C_4O_4)\ (2a) \xrightarrow{\sim 265^\circ C} X \end{array}$$

$$\text{(iii)}\quad \begin{array}{l} [Cd(eten)_2(H_2O)_2]C_4O_4\ (3) \xleftrightarrow[H]{87\text{–}110^\circ C} Cd(eten)_2(C_4O_4) \xrightarrow{190\text{–}235^\circ C} \\ Cd(eten)(C_4O_4)\ (3a) \xrightarrow{268\text{–}298^\circ C} Cd(eten)_{0.5}(C_4O_4) \xrightarrow{\sim 300^\circ C} X \end{array}$$

$$\text{(iv)}\quad \begin{array}{l} [Cd(pren)_2(H_2O)_2]C_4O_4 \xleftrightarrow[H]{80\text{–}110^\circ C} Cd(pren)_2(C_4O_4) \xrightarrow{170\text{–}210^\circ C} \\ Cd(pren)_{1.5}(C_4O_4) \xrightarrow{250\text{–}265^\circ C} Cd(pren)(C_4O_4)\ (4a) \xrightarrow{\sim 230^\circ C} X \end{array}$$

$$\text{(v)}\quad \begin{array}{l} [Cd(ipren)_2(C_4O_4)]\ (5) \xrightarrow{200\text{–}240^\circ C} Cd(ipren)_{1.5}(C_4O_4) \xrightarrow{250\text{–}265^\circ C} \\ Cd(ipren)(C_4O_4)\ (5a) \xrightarrow{\sim 264^\circ C} X \end{array}$$

$$\text{(vi)}\quad \begin{array}{l} [Cd(pn)_2(H_2O)_2]C_4O_4\ (6) \xleftrightarrow[H]{90\text{–}115^\circ C} Cd(pn)_2(C_4O_4) \xrightarrow{175\text{–}210^\circ C} \\ Cd(pn)(C_4O_4)\ (6a) \xrightarrow{274\text{–}300^\circ C} Cd(pn)_{0.5}(C_4O_4) \xrightarrow{\sim 302^\circ C} X \end{array}$$

$$\text{(vii)}\quad \begin{array}{l} [Cd(ibn)_2(H_2O)_2]C_4O_4\ (7) \xleftrightarrow[H]{92\text{–}122^\circ C} Cd(ibn)_2(C_4O_4) \xrightarrow{198\text{–}243^\circ C} \\ Cd(ibn)(C_4O_4)\ (7a) \xrightarrow{280\text{–}308^\circ C} Cd(ibn)_{0.5}(C_4O_4) \xrightarrow{\sim 310^\circ C} X \end{array}$$

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

Scheme 1

We tried to isolate intermediates in the solid state in pure form but succeeded the syntheses of $CdLC_4O_4$ only. They are stable in an open atmosphere and are non-electrolyte. IR-spectra (Fig. 1) suggest that the squarate anion is involved in coordination but the mode of coordination is not defined. To characterize them properly we tried to have single crystals but our attempts did not materialize. However, as Cd(II) may easily adopt octahedral geometry, specially in presence of strong field ligands like diamine and squarate, the squarate mono(diamine) complexes, $CdLC_4O_4$ should have polymeric structure where each Cd(II) is in octahedral environment having N_2O_4-chromophore originated from one diamine molecule and squarate moiety acting as tetradentate bridging ligand. Here it is to note that monodiamine complexes, MLX_2 (M=Ni(II), Cu(II), Zn(II) or Cd(II); X=Cl^-, Br^-, I^-, $0.5SO_4^{2-}$, $0.5SeO_4^{2-}$ etc.) are known and most of them have been reported to be synthesized from solution as well as in the solid state. But synthesis of analogous complexes with squarate anion from solution is not possible and pyrolytic method, as we reported earlier [13, 14] and here also is the only way to prepare them.

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

Complex	ν(C=O)	ν(C=O)	ν[(C–C)+(C–O)]
$[Cd(en)_3]C_4O_4$	1702 s	a	1540 vs, br, 1452 w
$Cd(en)(C_4O_4)$	1750 w	1611 m	1421, 1503 vs, br
$[Cd(meen)_2(H_2O)_2]C_4O_4$	1704 s	a	1540 vs, br, 1455 w
$Cd(meen)(C_4O_4)$	1783 w	1602 m	1486, 1493 vs, br
$[Cd(eten)_2(H_2O)_2]C_4O_4$	1700 s	a	1538 vs, br, 1435 w
$Cd(eten)(C_4O_4)$	1785 w	1622 m	1493 vs, br
$[Cd(pren)_2(H_2O)_2]C_4O_4$	1702 s	a	1540 vs, br, 1450 w
$Cd(pren)(C_4O_4)$	1762 w	1603 m	1494 vs, br, 1443 w
$[Cd(ipren)_2(C_4O_4)]$	1700 m	1620 m	1538 vs, br, 1470 w
$Cd(ipren)(C_4O_4)$	1760 w	1613 m	1484 vs, br, 1441 w
$[Cd(pn)_2(H_2O)_2]C_4O_4$	1702 s	a	1538 vs, br, 1452 w
$Cd(pn)(C_4O_4)$	1742 w	1600 m	1493 vs, br, 1468 w
$[Cd(ibn)_2(H_2O)_2]C_4O_4$	1710 s	a	1529 vs, br, 1456 w
$Cd(ibn)(C_4O_4)$	1755 w	1602 m	1476 vs, br

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}

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