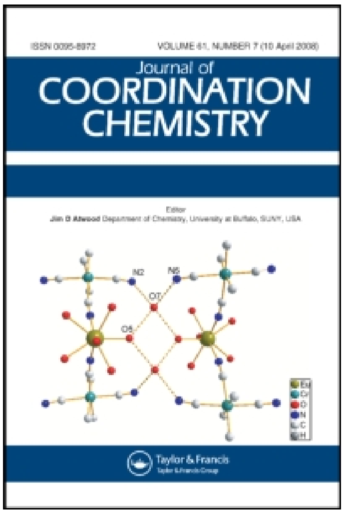

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Synthesis and spectroscopic study of 2-butenedioic acid (Z)-monophenyl ester and its ethereal oxygen coordinated complexes with Th(IV) and Ce(IV)

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Synthesis and spectroscopic study of 2-butenedioic acid (Z)-monophenyl ester and its ethereal oxygen coordinated complexes with Th(IV) and Ce(IV)

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2-Butenedioic acid (Z)-monophenyl ester and its complexes with tetravalent thorium and cerium have been synthesized and characterized by means of elemental analysis, TG-DTA, IR, ^{1}H NMR and ^{13}C NMR spectra. Chemical analysis and TG-DTA analysis indicated that the complexes possess the formula: $ML_2(OH)_2$ ($M = Th$ or Ce; $L =$ (Z)-monophenyl ester-2-butenedioate ion). The spectroscopic studies showed that besides the bidentate carboxylate bonded to the central tetravalent metal ions, the ethereal oxygen also coordinated. This was indicated by a higher wave number shift of $\nu_{C=O}$ in the complexes than that of free ligand and its sodium salt, and a remarkable upfield chemical shift of carbon atom (C-8) in the *p*-position of ethereal oxygen substituted phenyl.

Keywords: Butenedioic acid (Z)-monophenyl ester; Spectroscopic characterization; Ethereal oxygen coordination; Thorium; Cerium; Complexes

1. Introduction

Derivatives of 2-butenedioic acid, such as its alkyl esters [1–3], possess a conjugated structure and have been widely applied as potential catalysts [4], semiconductors, photoresist devices, and can improve the stability of polymers [5, 6]. Some 2-butenedioic acid monoalkyl esters form quite strong coordination bonds with alkali and alkaline earth metals, such as Li^+, Ca^{2+} and Mg^{2+} etc., giving excellent antibacterial and anstatic actions [7].

Investigations of monophenyl ester compounds [8–11], such as pentanedioic acid monophenyl ester and 3,3-diethyl-pentanedioic acid monophenyl ester, have been carried out, but analogues of 2-butenedioic acid monophenyl ester and its metal complexes have not been reported. As part of our continuing investigation into the preparation of lanthanide and actinide compounds with the derivatives of 2-butenedioic acid, we report here the synthesis and spectroscopic study of the 2-butenedioic acid (Z)-monophenyl ester and its ethereal oxygen coordinated complexes with Th(IV) and Ce(IV).

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The results indicate that the highly conjugated polydentate ligand can form a chelate ring with the center metal ions in which the ethereal oxygen and the bidentate carboxylate group of the ligand coordinate to the central metal ions, but the carbonyl oxygen is not involved in coordination. The formation of this unusual coordination bond can be attributed to the stronger electron withdrawing of phenyl, which makes the ethereal oxygen more electron rich than the carbonyl oxygen in complexes of typical alkyl ester with metal ions.

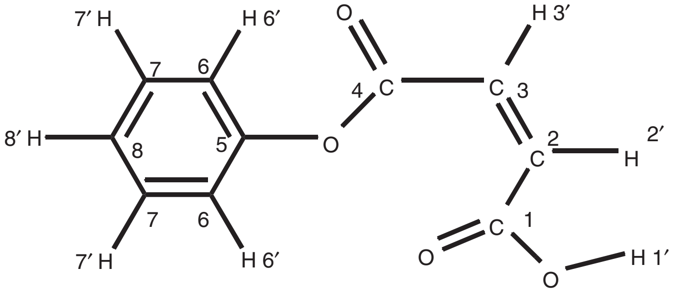
2. Experimental

2.1. *Materials and instruments*

Maleic anhydride, phenol, dried pyridine, thorium nitrate and ammonium ceric nitrate were of analytical grade and used without further purification. Vibrational spectra were recorded on a Nicolet 170SXET-IR spectrometer; thermal analysis was carried out on a PCT-2A thermal balance; elemental analyses were obtained with a Carlo Erba 1106 elementary analysis instrument; NMR data were collected on a Mercury Plus-300BB nuclear magnetic resonance apparatus with Me_4Si (TMS) as internal standard.

2.2. *Synthesis of ligand*

Maleic anhydride 1.47 g (15 mmol) and 1.41 g (15 mmol) phenol were put in a round bottom flask with a condenser and then heated until it melted while 0.2 mL dried pyridine (catalyst) was added dropwise under stirring. The reaction was processed for 5 h at 100°C then 0.1 mL dried pyridine was added again, and it continued to process for 1.5 h. After the carboxylic acid content decreased approximately 50% (detected by titration against standard KOH solution), the reaction was finished and the crude product of HL (HL represents the ligand, 2-butenedioic acid (Z)-monophenyl ester) was purified by column chromatography, using a mixture of ethyl acetate and petroleum ether (volume ratio = 1 : 7) as elutant. The product is white needle crystals, m.p. 120 ~ 122°C. The NMR spectra suggested that the product is *cis*. The structure is shown as scheme 1.



Scheme 1. The geometry optimization structure of HL using molecular mechanics (MM+).

2.3. *Synthesis of complexes*

HL (0.3072 g, 1.6 mmol) was dissolved in 25 mL 95% ethanol and stirred at room temperature while an acidic aqueous solution ($pH \approx 1$) containing 0.4 mmol $Th(NO_3)_4$ or $(NH_4)_2Ce(NO_3)_6$ was added dropwise. The mixtures were kept stirring for 48 h, and a white, or a brown, product was formed for the Th(IV) or Ce(IV) system, respectively. The solid precipitates were isolated from solution by centrifugation, then washed with distilled water several times to remove the nitrate radical and other impurities present, and finally washed with ethanol. Purification was carried out using DMSO and alcohol, but crystals were not obtained. Both complexes are insoluble in water, ether and ethanol, slightly soluble in chloroform, and readily soluble in DMSO and DMF.

2.4. *Chemical analysis procedure*

The metal contents were determined by volumetric titration [12] of EDTA using xylenol orange as indicator. A known amount of complex was decomposed with $3 \sim 5$ mL of 1 : 1 (volume ratio) concentrated nitric acid and perchloric acid under heating. The thorium content was titrated directly against a standard EDTA solution at $pH \approx 2$; the cerium decomposed into the corresponding Ce^{3+} salt, the excess acids and the ligand decomposed on heating. The Ce^{3+} content was carried out by standard procedures, that is, in a $pH \approx 5.5$ buffer solution, titrated with a standard EDTA solution, using xylenol orange as indicator. In order to avoid Ce^{3+} to be oxidized to Ce(IV) by air in the process, a little solid ascorbic acid was added before titration. The C, H and N contents were determined by elementary analysis instrument.

3. Results and discussion

3.1. *Chemical analysis of the complexes*

From the data listed in table 1, we can see that the complexes are formed in the ratio $M/L = 1:2$. The hydroxide ligands and (Z)-monophenyl ester-2-butenedioate ion in the complexes is due to the strong hydrolysis tendency of the tetravalent ions [13] and the steric hindrance of the ligand, which makes it difficult to form a $M/L = 1:4$ composition.

Table 1. Elemental analysis of the complexes.

Ligand HL		C% 62.34 (Calcd 62.50)	H% 3.75 (Calcd 4.17)
Complex **1** $ThL_2(OH)_2$	M% 36.35 (Calcd 35.80)	C% 37.56 (Calcd 37.03)	H% 2.42 (Calcd 2.47)
Complex **2** $CeL_2(OH)_2$	M% 25.20 (Calcd 25.18)	C% 42.95 (Calcd 43.17)	H% 2.52 (Calcd 2.88)

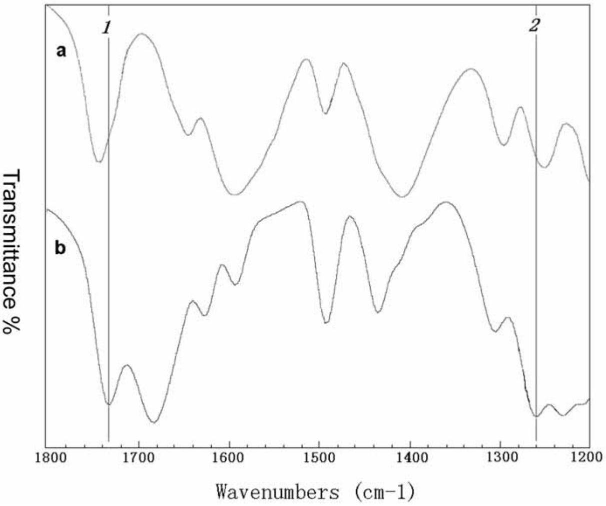


Figure 1. FTIR spectra of the complex of Th(IV) (a) and the ligand HL (b).

3.2. *IR analysis*

The IR spectra of both complexes (KBr discs) are very similar, indicating similar structure, but quite different from that of free ligand HL. Figure 1 is the FTIR spectra of the complex of Th(IV) (a) and the ligand HL (b).

Compared with free ligand, the vibration band of ester group $\nu_{CO(E)}$ in the complex has shifted to higher wavenumber (1741 cm^{-1} from 1732 cm^{-1} see line 1), and the ν_{C-O-Ar} band shifted from 1258 cm^{-1} to lower wavenumber 1247 cm^{-1} (see line 2), indicating coordination of the ethereal oxygen to the tetravalent metal ions [14]. Formation of the coordination bond of ethereal oxygen with the metal diminishes the charge density on the ethereal oxygen and decreases the force constant k of C–O–Ar, causing the results mentioned above [14, 15].

Another obvious change is that the three characteristic absorption bands of the carboxylic acid of the ligand at 2878 cm^{-1} (ν_{O-H}), 1682 cm^{-1} ($\nu_{C=O}$, s) and 943 cm^{-1} (δ_{O-H},w) are changed in the complexes. As shown in figure 1, in Th(IV) complex the intense antisymmetric carboxylate stretch at 1591 cm^{-1} ($\nu_{asCOO(A)}$) and the symmetric stretch at 1405 cm^{-1} ($\nu_{sCOO(A)}$), are separated by 186 cm^{-1}.

Comparing infrared spectra of the Th(IV) complex with the corresponding sodium salt NaL shows that the symmetry of the carboxylate group in the complex is *C2v*, the same symmetry as the free ion, whereas the $\Delta\nu$ (186 cm^{-1}, $\Delta\nu = \nu_{asCOO(A)} - \nu_{sCOO(A)}$) is smaller than that for the NaL (196 cm^{-1}) indicating a bidentate chelate coordination mode for the carboxylate group in the complex [16]. The Ce(IV) complex has a smaller splitting ($\Delta\nu = 145\,cm^{-1}$) of the CO_2-stretching frequency, an indication of bidentate coordination [17, 18]. In the range 3420 ~ 3440 cm^{-1}, the strong bands from OH vibrations are broadened from hydrogen bonding of the type $-OH \cdots O$.

3.3. *Thermal analysis*

The simultaneous TG-DTA curves of Th(IV) and Ce(IV) complexes were carried out using α-Al_2O_3 as reference material, samples of about 10 mg were placed in a crucible and heated at the rate of 10°C min^{-1} in air from room temperature to 700°C at ambient pressure. The determination indicates that the complexes are rather stable with no obvious weight loss under 250°C. This is consistent with chemical analysis, showing no H_2O in the complexes. TG-DTA curve shows that the Th(IV) complex commences decomposition at 353°C. For the cerium complex, a strong exothermic peak appears at ~300°C with a visible weight loss in the corresponding TG curve at 290 ~ 322°C. These analyses suggest that the Th(IV) complex is more stable than the Ce(IV) complex [19]. The total weight losses for complexes of Th and Ce are 59.08% (Calcd 59.26%) and 68.95% (Calcd 69.06%), respectively, suggesting that the final decomposition products for both complexes are metal dioxides.

3.4. *NMR analysis*

The ^{1}H and ^{13}C NMR data of HL and the complexes are listed in tables 2 and 3, respectively [20]. The complexes were dissolved in $(CD_3)_2SO$ and HL was dissolved in $CDCl_3$.

The single peak of –COOH in the free ligand located at δ 10.810 disappears in the ^{1}H NMR spectra of the complexes, which suggests that the carboxylic acid group is deprotonated in the complexes, consistent with the chemical analysis and IR analysis. The chemical shifts of H-2′ and H-3′ are markedly upfield in the complexes due to the carboxylate enhancing the shielding, and increasing electron density of H-2′ and H-3′. The coupling constants of H-2′ and H-3′ are the same in the ligand and in the complexes indicating that the double bond configuration remains in the complexes.

In the ^{13}C NMR data of HL and the complexes listed in table 3, the chemical shifts of C-1, C-2, C-3, C-4 and C-8 change. The chemical shifts of C-1 and C-4 shift downfield, and the chemical shifts of C-2 and C-3 shift upfield, consistent with the ^{1}H NMR analysis showing the oxygen atoms attached to C-1 and C-4 take part in coordination. The aromatic ring has four different carbon atoms: the *ipso* carbon (C-5) is of low intensity, a little downfield from the ligand; the two *ortho* carbons (C-6) are identical with each other as are the two *meta* carbons (C-7); they are the high intensity lines slightly downfield from the ligand. A notable difference between ligand and complexes is that the chemical shift of the *para* carbon (C-8) *para* to the ethereal oxygen in the complexes changes from δ 126.35 to δ 143.42 ~ 143.21. Usually the long-distant influence of an aromatic ester is weak, so the shift is ascribed to the decrease of electron density on ethereal oxygen bonded to the aromatic ring when the complex is formed [21, 22].

Each complex contains two ligand ions and two hydroxyl ions coordinated with the central ion. The ligand coordinates as a tridentate chelate, forming a seven-member chelate ring. The coordination number for each metal is 8. A proposed structure for the complex is shown in scheme 2.

4. Conclusions

The 2-butenedioic acid (Z)-monophenyl ester and its ethereal oxygen coordinated complexes with tetravalent thorium and cerium have been synthesized from an acidic

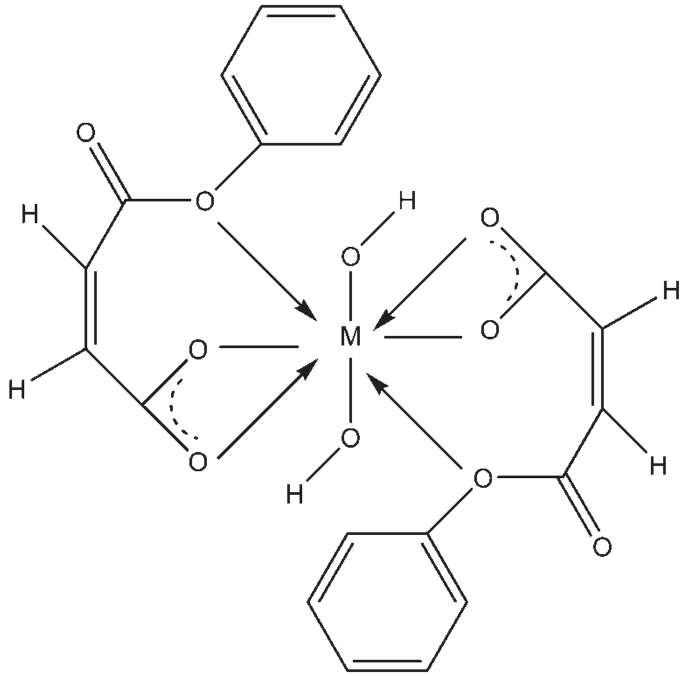
Table 2. ^{1}H NMR (300 MHz) data of HL and $ThL_2(OH)_2$ (assignment, δ_H).

Complexes	**8′**	**7′**	**6′**	**3′**	**2′**	**1′**
HL	7.255 ~ 7.301 (m,1H)	7.393 ~ 7.445 (m, 2H)	7.144 ~ 7.17 (d, J = 7.8 Hz, 2H)	7.022 ~ 7.074 (d, J = 15.6 Hz,1H)	7.134 ~ 7.186 (d, J = 15.6 Hz, 1H)	10.810 (s,1H)
$ThL_2(OH)_2$	7.222 ~ 7.248 (d, J = 7.8 Hz, 1H)	7.287 ~ 7.312 (m, 2H)	7.015 ~ 7.041 (d, J = 7.8 Hz, 2H)	6.722 ~ 6.774 (d, J = 15.6 Hz, 1H)	6.836 ~ 6.888 (d, J = 15.6 Hz, 1H)	/ /
$CeL_2(OH)_2$	7.105 ~ 7.131 (d, J = 7.8 Hz, 1H)	7.234 ~ 7.259 (m, 2H)	6.860 ~ 6.886 (d, J = 7.8 Hz,2H)	6.651 ~ 6.702 (d, J = 15.3 Hz,1H)	6.762 ~ 6.814 (d, J = 15.6 Hz, 1H)	/ /

Table 3. 13C NMR (75 MHz) data of HL and $ThL_2(OH)_2$ (assignment, δ_C).

Complexes	**8**	**7**	**6**	**5**	**4**	**3**	**2**	**1**
HL	126.35	129.57	121.19	150.14	163.06	134.13	135.05	170.00
$ThL_2(OH)_2$	143.42	129.52	121.69	150.23	164.06	126.02	127.81	172.02
$CeL_2(OH)_2$	143.21	129.25	121.52	150.21	164.03	125.54	127.29	171.70
$\Delta\delta_{Th^*}$	−17.07	0.05	−0.50	−0.09	−1.00	8.11	7.24	−2.02
$\Delta\delta_{Ce}$	−16.86	0.32	−0.33	−0.07	−0.97	8.59	7.76	−1.70

* $\Delta\delta = \delta_{HL} - \delta_{ML_2(OH)_2}$, M = Th or Ce.



Scheme 2. The structure of complexes M = Th(IV) or Ce (IV) (hydrogen atoms bonded to the aromatic ring are omitted for clarity).

medium and well characterized by means of elemental analysis, TG-DTA, IR and NMR spectra. Chemical analysis indicated that these complexes possess the same formula, $ML_2(OH)_2$. The results showed that besides the bidentate carboxylate bonded to the central tetravalent metal ions, the ethereal oxygen in the ligand also coordinated. The carbonyl oxygen did not take part in coordination, as observed in complexes containing ester as ligands.

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