A Dimeric Cerium(III) Acetylacetonate Complex Containing Intramolecular and Intermolecular Hydrogen Bond

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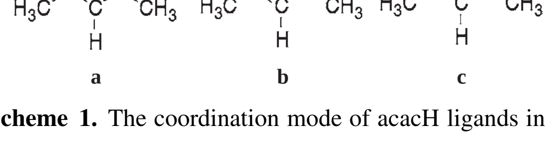
A dimeric [Ce(acac)$_3$(acacH)$_2$] (acacH = acetylacetone) complex has been synthesized. The crystal structure showed that the complex contains intramolecular H-bond and intermolecular H-bond formed through the neutral enol acetylacetone unidentate ligands.

Metal β-diketonate complexes, in particular the complexes of acetylacetone (acacH), probably have a more extensively examined chemistry than other chelate system.[1] It is well known that acetylacetone consists of keto and enol tautomers. Under appropriate conditions the enolic hydrogen atom of the acetylacetone may be replaced by a metal cation to produce a six-membered metallocycle, thereby shifting the keto–enol equilibrium in favor of the chelated enolate anion form in metal acetylacetonate complexes.[2] Previous studies on metal acetylacetonate complexes presented an excellent review on the works up to 1990,[3] in which the ligand occurs various coordination modes, most of them accepted the enolate anion. However, earlier studies of several transition-metal acetylacetonate complexes have shown that acetylacetone molecules as neutral ligands could be coordinated to metal atoms as keto and enol tautomers.[4] Acetylacetone with the ability to chelate the cerium ion is proved to be very adept at a monoanionic bidentate oxygen donor in the enol form.[5] In this paper, the complex of [Ce(acac)$_3$(acacH)$_2$] (**1**) was synthesized. It is interesting that acetylacetone molecule as a neutral ligand coordinates to Ce$^{\mathrm{III}}$ through only one oxygen atom, as it is shown in Schemes 1b and 1c, the enol tautomers can be regarded not only as hydrogen-bond acceptors but also as hydrogen-bond donors. Two [Ce(acac)$_3$(acacH)$_2$] molecules are linked together by a pair of intermolecular hydrogen-bonds. Therefore, the complex with new structure features was formed by simple ligands.

A freshly distilled acetylacetone (20 mL) was neutralized with 30% (v/v) $NH_3 \cdot H_2O$ (20 mL), the mixture was added to an aqueous solution of $Ce(NO_3)_3 \cdot 6H_2O$ (6.91 mmol). After stirring for 6 h at room temperature, the resulting yellow weak, column-like crystals of **1** were obtained from a dark brown solution (Yield: 63%). Anal. Found: C, 46.89; H, 6.02; Ce, 22.23%. Calcd for $C_{25}H_{37}CeO_{10}$: C, 47.09; H, 5.84; Ce, 21.97%. Infrared (KBr, cm^{-1}): 3337(m), 3189(m), 1596(s), 1514(s), 1403(s), 1304(s), 1011(m), 914(w), 754(m), 523(w).



Scheme 1. The coordination mode of acacH ligands in **1**.

Single-crystal X-ray analysis[6] has revealed that Ce$^{\mathrm{III}}$ is coordinated from eight oxygen atoms of three bidentate acac ligands and two unidentate acacH ligands in a distorted square antiprism (Figure 1). The distortion of the square antiprism was possibly attributed to the presence of different coordination modes of the ligands (Scheme 1) bonded to the same metal atom, just similar to the case in [Ce(acac)$_3$(H$_2$O)$_2$].[7] Two neutral acacH molecules as unidentate ligands are coordinated to Ce through only carbonyl oxygen atoms. The metal–chelate ring containing O(6) and O(5) are planar, because the sum of the interior angles are 719.86°, as compared with 720° required for planarity. The other two chelated acac ligand rings are folded, the folding angles are 28.03 and 27.09°.

The Ce$^{\mathrm{III}}$–O bond lengths vary from 2.426(3) to 2.519(3) Å among them the bond lengths from Ce$^{\mathrm{III}}$ to O(7) and O(9) of the unidentate acacH are slightly longer (mean 2.502 Å) than those from Ce$^{\mathrm{III}}$ to O(1) and O(6) of the chelate acac groups (mean 2.463 Å). The unidentate acacH molecules have a long C(19)–O(8) and C(24)–O(10) bonds, due to the O(8) and O(10) also binding to H atoms. The O–H group of one acacH participates in intramolecular hydrogen bond O(8)–H(8)···O(7) 2.735(4) Å. A similar observation was reported for the [U(C$_5$H$_7$O$_2$)$_2$-(C$_5$H$_8$O$_2$)O$_2$][8] and MnBr$_2$(acacH)$_2$.[9] A notable feature is that the dimeric complex also exists a pair of intermolecular hydrogen bonds O(10)–H(10)···O(4) 3.064(5) Å, which link two

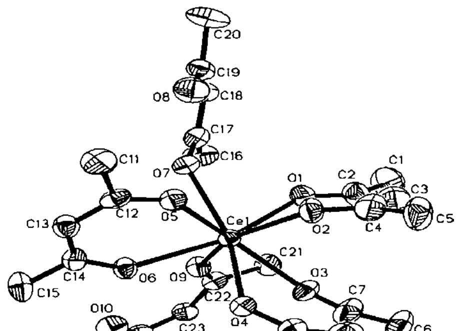


Figure 1. The molecular structure of **1** showing the atom numbering scheme and 35% displacement ellipsoids. H atoms have been omitted. Selected bond distances (Å) and angles (°): Ce(1)–O(2), 2.426(3); Ce(1)–O(3), 2.453(3); Ce(1)–O(6), 2.460(3); Ce(1)–O(1), 2.462(3); Ce(1)–O(5), 2.478(3); Ce(1)–O(9), 2.489(3); Ce(1)–O(4), 2.490(3); Ce(1)–O(7), 2.519(3); O(8)–C(19), 1.346(5); O(10)–C(24), 1.342(5); C(12)–O(5)–Ce(1), 136.0(3); C(14)–O(6)–Ce(1), 137.3(3); O(6)–Ce(1)–O(5), 69.96(9);

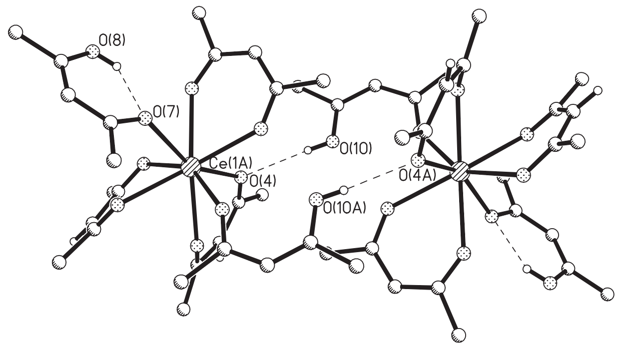


Figure 2. Hydrogen-bonded dimeric unit **1** (Thin dashed line indicate the O–H···O hydrogen bond). Symmetry transformations used to generate equivalent atoms: #1 $-x, -y+1, -z+2$.

monomer to form a cyclic hydrogen-bonded dimer (Figure 2). The nearest intermolecular Ce–Ce distance is 7.976 Å. Each dimer is discrete, without further interactions to neighboring dimers. Two hydrogen-bonding interactions form the chair-shaped 16-membered ring.

We believed that this is the first reported intermolecular hydrogen-bonded dimer found in lanthanide acetylacetonate complexes without other ancillary ligands. It should be pointed out that, previously reported compounds containing neutral acacH, such as $CoCl_2$(acacH), $ZnCl_2$(acacH), $NiBr_2(acacH)_2$,[5] $CoBr_2$(acacH),[10] $[Mg(acacH)_2{\cdot}(H_2O)_2](ClO_4)_2$,[11] involve in ketonic molecules, which is the major difference from the present complex. The formation of the intermolecular hydrogen bonds in the present complex further stabilized the coordinated neutral enolic molecule. This was also the reason for substituting neutral enolic molecule for the coordinated H_2O in $[Ce(acac)_3(H_2O)_2]$ and resulting in the formation of the present complex $[Ce(acac)_3(acacH)_2]$. Therefore, using ligand capable of forming intermolecular hydrogen bond to substitute the simple ligand in the single complex would possibly provide a new way for preparing supermolecular lanthanide complex system. By changing the center metal ion in the complex, for example, substituting Eu^{3+} or Tb^{3+} for Ce^{3+}, a new way to study how the coordinated neutral enolic molecules influence the luminescence of the rare earth ions can be found. This work is in progress now in our laboratory.

The thermal decomposition behavior of the complex was studied in the temperature range of 20–900 °C (Figure 3). The TGA curve shows that the first weight loss of 33.64% from 90 to 153 °C, corresponds to the loss of the two acacH ligands (calculated: 31.40%). The next weight loss of 15.24% between 154 and 259 °C possibly corresponds to the loss of the one chelate acac ligand (calculated: 15.54%). These results indicated that enol chelate ligand is more stable than the enol unidentate ligand. The third step weight loss of 12.11% between 259.44 and 367.76 °C liberates another acac ligand. Then, the last acac ligand is lost between 368 and 421 °C, and the residue is Ce^{IV} oxide, which is confirmed by XPS measurement (see Supporting Information).[12]

In summary, we provide a new way to prepare dimeric lanthanide complex and a new structure of dimeric Ce^{III} acetylacetonate complex containing enol acacH molecules.

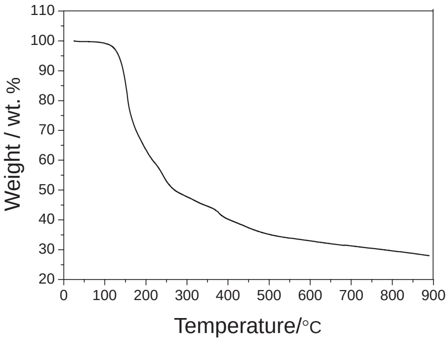


Figure 3. TGA traces of the thermal decomposition of **1**.

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6 Crystal data for **1**: $C_{25}H_{37}CeO_{10}$, $M_r = 637.67$, monoclinic, space group $P2(1)/c$, $a = 14.778(3)$, $b = 11.618(2)$, $c = 17.513(4)$ Å, $\beta = 95.58(3)°$, $V = 2992.7(10)$ Å^3, $Z = 4$, $D_{calcd} = 1.415$ g cm^{-3}, 6852 reflections collected, 3517 unique ($R_{int} = 0.120$), $R_1 = 0.0401$, $wR_2 = 0.0793$, GOF = 0.880. The intensity data was collected on a NONIUS KappaCCD diffractometer with Mo Kα radiation ($\lambda = 0.71073$ Å) at 293 K. Crystallographic data reported in this manuscript have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-612828. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

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12 Supporting Information is also available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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