

Formation and catalytic activity of novel water soluble di[ethylenediaminetetraacetato bis(N-oxido)] lanthanides



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ABSTRACT

Reaction of hydrogen peroxide with ethylenediaminetetraacetato lanthanides results in the formation of water-soluble isomorphous N-oxido ethylenediaminetetraacetato lanthanides $K_5[Ln(edtaO_2)_2] \cdot 12H_2O$ [$Ln = La$ (**1**), Ce (**2**), Nd (**3**)], $H_4edta =$ ethylenediaminetetraacetic acid $C_{10}H_{16}O_8N_2$) in weak basic solution, where lanthanide ions are octa-coordinated by two quadrantate N-oxido edta ligands, resulting in a distorted anti-tetragonal prism. Based on the comparisons of solid and solution ^{13}C NMR spectra, these compounds are fully dissociated in solution. Catalytic reaction of $K_5[La(edtaO_2)_2] \cdot 12H_2O$ shows 96% conversion for the reaction of pyridine to pyridine N-oxide at 70 °C.

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Peroxo lanthanides are the major species of lanthanide in neutral solution with hydrogen peroxide [1]. They are important in the process of catalytic reaction with rare earth oxide like hydroxylations of benzene and selective oxidation of low alkane [2–4]. When hydrogen peroxide exists, lanthanides are suggested to form peroxo lanthanides. Several factors such as molar ratio of $Ln: H_2O_2$, acidity, solvent, ligand and temperature have been found to affect the formation of peroxo lanthanides. However, more details of isolation of the peroxo lanthanides are limited. Only a well-defined side-on-bonded superoxo $Sm(\eta^2-O_2)$ is reported [5]. There are also a few lanthanide complexes containing $\mu-\eta^2:\eta^2$ -peroxo group bridged with heteroligand environments [6–14]. The conversions are unknown for the peroxo group. This is probably due to the instability of the system and the slow formation of the anions. Moreover, photoinduced formation of lanthanide peroxide has been discovered by the laser excitation on the Ln_2O_3 surface under oxygen atmosphere [15]. Here we have succeeded in the isolations of N-oxido edta lanthanides in presence of excess hydrogen peroxide and edta lanthanides $K[Ln(edta)(H_2O)_3] \cdot 5H_2O$ ($Ln = La, Ce, \text{ and } Nd$). The later have been also used as starting materials for the preparation of dimeric lanthanide citrate and malate with edta in our previous report [16]. An interesting addition of peroxo group into less soluble edta lanthanides forms water-soluble di-[ethylenediaminetetraacetato bis(N-oxido)] lanthanides $K_5[Ln(edtaO_2)_2] \cdot 12H_2O$, which serves as the reaction products of $Ln(\eta^2-O_2)$ with edta. The syntheses, infrared and ^{13}C NMR spectra, and structural characterizations of the three novel lanthanides

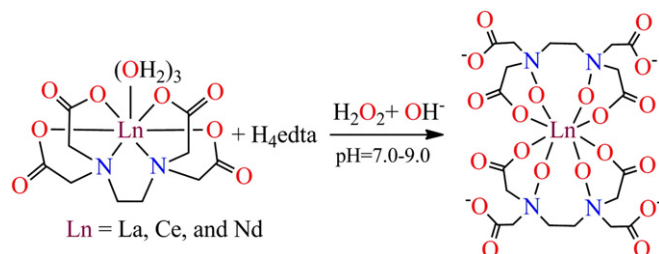
$K_5[Ln(edtaO_2)_2] \cdot 12H_2O$ [$Ln = La$ (**1**), Ce (**2**), Nd (**3**)] are reported, where $K_5[La(edtaO_2)_2] \cdot 12H_2O$ was used as catalyst for the conversion of pyridine to pyridine N-oxide.

Unlike direct reaction between metal salt with N-oxide ligand [19–22], edta lanthanide $K[Ln(edta)(H_2O)_3] \cdot 5H_2O$ and hydrogen peroxide were used as reactants for the preparations of N-oxido edta lanthanides $K_5[Ln(edtaO_2)_2] \cdot 12H_2O$ in aqueous solution at pH 7.0–9.0 [17,18]. Under an optimal condition of pH 8, $K_5[Ln(edtaO_2)_2] \cdot 12H_2O$ can be obtained in yields of 53% (La), 55% (Ce), and 69% (Nd) respectively. The molar ratio of $K[Ln(edta)(H_2O)_3] \cdot 5H_2O: H_2O_2$ was maintained in 1:5. Syntheses and conversions of the peroxo lanthanides are depicted in Scheme 1. pH control and the concentration of hydrogen peroxide are critical for the formation of N-oxido lanthanides.

Crystal structures of $K_5[Ln(edtaO_2)_2] \cdot 12H_2O$ consist of di-[ethylenediaminetetraacetato bis(N-oxido)] lanthanide anions, potassium cations, and lattice water molecules. The anion structure of **1** was shown in Fig. 1. Those of **2** and **3** were shown in Figs. S1 and S2. Each lanthanide cation is octa-coordinated by two edtaO₂ ligands and displays as a distorted anti-tetragonal prism as shown in Fig. 2. Each N-oxido edta coordinates to lanthanide cation with two N-oxide atoms and two carboxy groups.

Selected bond distances of the title compounds are listed in Table 1. In monomer **1**, the Ln–O bond distances are between 2.427(3) and 2.537(3) Å, where La–O bonds of carboxy groups are longer [La1–O1, 2.537(3); La1–O5, 2.486(3); La1–O11, 2.515(4); La1–O15, 2.500(4) Å] than those of N-oxide [La1–O9, 2.427(3); La1–O10, 2.484(3); La1–O19, 2.500(3); La1–O20, 2.445(3) Å]. The similar results can be found in compounds **2** and **3**. It is worth noting that, for all three complexes, the N–O bond distances (N-oxide) range from 1.396(5) to 1.411(5) Å with a mean value of 1.402(5) Å. This is similar to the N–O

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Scheme 1. Formation of water soluble N-oxido ethylenediaminetetraacetato lanthanides $\text{K}_5[\text{Ln}(\text{edtaO}_2)_2] \cdot 12\text{H}_2\text{O}$.

distance [1.413(7) Å] as reported [21]. Based on Table S1, the Ln–O bond distances [La–O, 2.509(4); Ce–O, 2.493(5); Nd–O, 2.458(5) Å] decrease with the increase of atomic number. This is the result of lanthanide contraction.

Solid and solution ^{13}C NMR spectra of **1** were shown in Fig. 3 and its solution ^1H NMR spectrum in Fig. S3. The solid state ^{13}C NMR spectra of $\text{K}_5[\text{La}(\text{edtaO}_2)_2] \cdot 12\text{H}_2\text{O}$ (**1**) give five peaks at $\delta = 54.2, 65.9, 70.4, 170.4$ and 171.2 ppm. It is interesting to note that all of the four CH_2 moieties from acetate groups occur as two single peaks at 70.4 and 65.9 ppm, which correspond to the two carboxy groups coordinated to La, and the other two groups remain free as internal reference. Obvious downfield shift ($\Delta\delta$ 3.5 ppm) is observed after coordination. Moreover, the CH_2 groups of N-bound methylene moiety ($\delta = 54.2$ ppm) are not differentiated, which confirms the presence of N–O groups in the complex. The presence of two ^{13}C peaks at 170.4 and 172.1 ppm also implies that two carboxy groups coordinate to La with downfield shift $\Delta\delta$ of 1.7 ppm, while the other two groups remain free. This is consistent with the structural analysis.

The solution ^{13}C NMR spectrum of $\text{K}_5[\text{La}(\text{edtaO}_2)_2] \cdot 12\text{H}_2\text{O}$ (**1**) only shows three peaks. The chemical shift (173.0 ppm) of carboxy groups in $[\text{edtaO}_2]^{4-}$ is similar to that of free $[\text{edtaO}_2]^{4-}$ (173.3 ppm). This may indicate the full dissociation of the complex in solution. The other two peaks at 70.5 and 59.2 ppm are ascribed to CH_2 groups of acetates and N-bound moieties respectively. Comparing the solution spectrum of **1** with free $[\text{edtaO}_2]^{4-}$ ligand, highfield shift for CH_2N ($\Delta\delta = -3.2$ ppm) and downfield shift for CH_2CO_2 ($\Delta\delta = 0.3$ ppm) can be found. The former is due to the binary effect of pulling electrons by quaternary nitrogen and the coordination of N-oxide.

IR spectra of $\text{K}_5[\text{Ln}(\text{edtaO}_2)_2] \cdot 12\text{H}_2\text{O}$ are shown in Fig. S5. Comparing with the free ligand at 1700 cm^{-1} , we found significant blue-shift for $\nu_{\text{as}}(\text{CO}_2)$ at $\sim 1620\text{ cm}^{-1}$. The bands ranging from

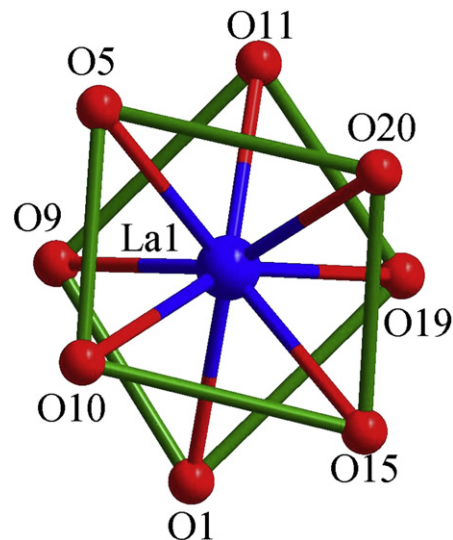


Fig. 2. Distorted anti-tetragonal configuration of La(III) cation.

1310 to 1400 cm^{-1} belong to $\nu_s(\text{CO}_2)$. Moreover, oxidation of the nitrogen atoms of the edta ligand is evidenced by the $\nu(\text{N}-\text{O})$ band at 900 cm^{-1} . In free ligand, the corresponding band appears at $\sim 890\text{ cm}^{-1}$ [21]. Thermal analysis of compound **1** was shown in Fig. S6. The weight loss of 6.41% below $223\text{ }^\circ\text{C}$ (calcd 6.04%) corresponds to the loss of four crystal water molecules/formula. The compound begins to decompose and degrade to $\text{K}_{10}\text{La}_2\text{O}_8$ at the higher temperature. The thermal behaviors of compounds **2** and **3** are similar.

The lanthanide edta N-oxide $\text{K}_5[\text{La}(\text{edtaO}_2)_2] \cdot 12\text{H}_2\text{O}$ was used for the catalytic conversion of pyridine to pyridine N-oxide [23,24]. In order to find suitable conditions for catalytic oxidation of pyridine, various parameters, such as amount of catalyst **1**, reaction time and temperature have been taken into considerations. Water is used as reaction media; this is due to the solubility of pyridine and catalyst. The molar ratio of pyridine: H_2O_2 was maintained in 1: 4. The reaction temperature had a great effect on the oxidation of pyridine as shown in Fig. 4. The conversion of pyridine increased with increasing temperature and reached the maximum at $70\text{ }^\circ\text{C}$. At the same temperature, the yield of pyridine N-oxide increased with the catalyst amount. More catalyst resulted in the precipitation and reduced the activity of the catalyst. Fig. S7 shows the solution ^{13}C NMR spectra of reaction mixture with time at $70\text{ }^\circ\text{C}$, the reaction could not be detected within 2 hours. After 9 hours, three peaks at 150.8, 140.4 and 127.1 ppm are assigned to the signals of pyridine, the other three peaks at 141.4, 134.9 and 129.9 ppm to ^{13}C NMR signal of pyridine N-oxide. The conversion of pyridine reached almost 100% after 24 hours without side product. The optimal molar ratio of catalyst $\text{K}_5[\text{La}(\text{edtaO}_2)_2] \cdot 12\text{H}_2\text{O}$ (**1**) was 0.67% (0.1 g) with respect to pyridine, and the molar ratio of pyridine to H_2O_2 was 1: 4 at $70\text{ }^\circ\text{C}$ for 24 hours. Catalytic conversion of lanthanum chloride gave 16%, while the solutions of $\text{K}_4(\text{edtaO}_2)$ [21] and $\text{K}[\text{La}(\text{edta})(\text{H}_2\text{O})_3] \cdot 5\text{H}_2\text{O}$ shown only 7% and 4% respectively. This shows that only edtaO_2^{2-} itself can not play a catalytic conversion role for the formation of pyridine N-oxide. Both lanthanide and edtaO_2^{4-} ions cooperatively catalyzes the conversion reaction of pyridine into N-oxide. $\text{K}_5[\text{La}(\text{edtaO}_2)_2] \cdot 12\text{H}_2\text{O}$ (**1**) showed a significant catalytic activity for the oxidation of pyridine with a yield of 96%.

New lanthanide complexes with N-oxide derivatives of ethylenediaminetetraacetate have been prepared and characterized. Conversion of N-oxide added a new reactivity for peroxo peroxo lanthanides. Moreover, $\text{K}_5[\text{La}(\text{edtaO}_2)_2] \cdot 12\text{H}_2\text{O}$ was a suitable catalyst for the catalytic oxidation of pyridine in high yield.

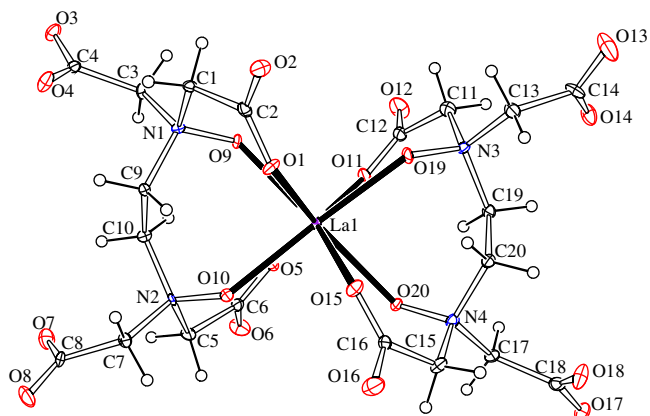


Fig. 1. ORTEP plot of the anion of monomeric $\text{K}_5[\text{La}(\text{edtaO}_2)_2] \cdot 12\text{H}_2\text{O}$ (**1**) at the 30% probability levels.

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