Novel Discrete Structure of Oxalate-bridged Heteronuclear Cr(III)-Nd(III) Complex

Narumi Sakagami* and Ken-ichi Okamoto
Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305

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A novel chromium(III)-neodymium(III) heteronuclear complex has been obtained by utilizing *unsym-cis*-[Cr(eddp)(ox)]$^-$ as a building block. From the X-ray analysis, it is revealed that this complex is tetranuclear in which the Nd(III) ion is bridged by three oxalates in the three Cr(III) units and three water molecules forming a nine-coordinate tricapped trigonal-prism geometry.

The chemistry of the heteropolynuclear complexes with the transition metal and the rare-earth metal has been interested in view of the magnetic and electronic properties.[1-4] Although many heteropolynuclear complexes have been reported and their magnetic properties have been investigated, the number of structurally characterized transition metal and rare-earth metal polynuclear complexes is still limited.[1-3,5,6] We have recently reported Cr$^{III}{}_2$Nd$^{III}{}_3$ pentanuclear complex containing carboxylate bridges of acetate and hydroxy bridges.[6] To obtain such heteronuclear complexes more effectively, it is useful to apply the strategy of "complexes as ligands". The oxalate ion is an efficient bridging ligand for the stepwise synthesis of polynuclear complexes. It is well-known that chromium(III) complexes are quite inert toward ligand substitution, allowing a good control over the reaction products. For these reasons, a mononuclear chromium(III) complex with one oxalate ligand, [Cr(eddp)(ox)]$^-$, (eddp = ethylenediamine-*N,N'*-dipropionate, ox = oxalate), is selected as a building block. Now we report the first oxalate-bridged tetranuclear Cr^{III}–Nd^{III} complex, [Nd{Cr(eddp)(ox)}$_3$(H$_2$O)$_3$]·12H$_2$O (**1**).

To a solution of *unsym-cis*-Na[Cr(eddp)(ox)]·3H$_2$O[7] (3.77 g, 9.0 mmol) in 10 cm^3 of H$_2$O was added NdCl$_3$·6H$_2$O (1.08 g, 3.0 mmol). Red crystals were obtained by standing the solution in the ethanol-acetone atmosphere at room temperature for a few days.[8] A well formed red crystal of [Nd{Cr(eddp)(ox)}$_3$(H$_2$O)$_3$]·12H$_2$O (**1**) was used for the X-ray analysis.[9,10]

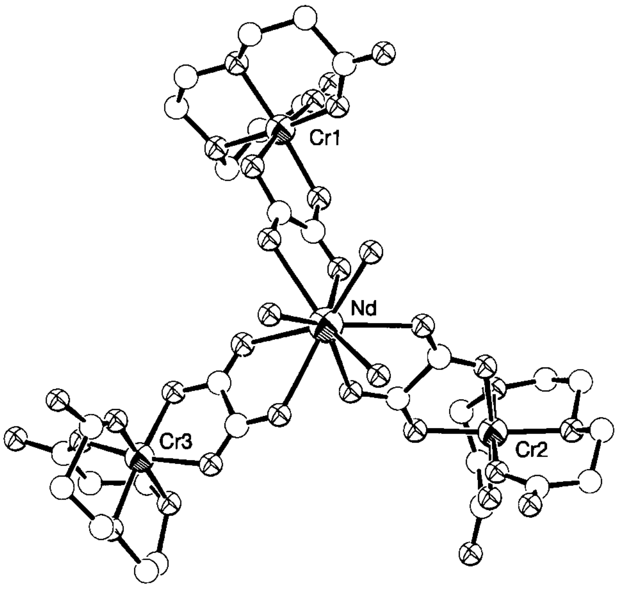

Figure 1. Molecular structure of **1**. Hydrogen atoms are omitted for clarity. Selected bond distances and angles (average): Nd–O(ox)(short), 2.48(1) Å; Nd–O(ox)(long), 2.59(1) Å; Nd–Ow, 2.50(1) Å; Cr–O(eddp), 1.91(2) Å; Cr–O(ox), 2.00(1) Å; Cr–N, 2.04(1) Å; O(ox)–Nd–O(ox)(chelate), 64.4(4)°; Ow–Nd–Ow, 77.9(1)°; O(ox)–Cr–O(ox), 81.7(4)°; N–Cr–N, 81(1)°.

The molecular structure of **1** is shown in Figure 1. This complex consists of discrete {Cr$_3$Nd} entities containing three *unsym-cis*-[Cr(eddp)(ox)]$^-$ units and one Nd atom. Most of the oxalate-bridged homo and hetero metal complexes are polymer[11-15] and only a few examples have been obtained as discrete molecules.[14(b),15-18] To our knowledge, this is the first structurally characterized discrete Cr^{III}–Ln^{III} complex. The Nd atom is coordinated by each two carboxy O atoms at the oxalate ligand of three [Cr(eddp)(ox)]$^-$ anions and three water molecules forming a nine-coordinate tricapped trigonal-prism geometry. Bond distances and angles are almost identified to those of Nd(III)-oxalate complexes.[14] The Nd–Ow(water) bonds are 2.48(2) to 2.52(2) Å. Three of the Nd–O(ox) distances are 2.46(2) to 2.50(2) Å, while three others are much longer, ranging from 2.57(2) to 2.61(2) Å. Each oxalate ligand in [Cr(eddp)(ox)]$^-$ is bonded to the Nd ion by a long and a short bond. Three longer bonds are situated on the tricapped position of the polyhedron and three shorter bonds and three Nd–Ow bonds are on the top and the bottom of the trigonal-prism, respectively. Three [Cr(eddp)(ox)]$^-$ units show almost the same structure and the same absolute configuration. All of them maintain the starting *unsym-cis* geometry, where one β-alaninate of the eddp coordinates at the out-of-plane ring and the other one coordinates at the in-plane ring. Additionally, this *unsym-cis* isomer can be referred to as the β(e-1) isomer.[19] That is, the absolute configurations of the coordinated asymmetric *sec-N* atoms in the both propionate rings are *R*, when the absolute configuration about the Cr(III) ion is Δ (Figure 2). Bond distances and angles around the octahedral Cr(III) ion are within the range of the general Cr(III) complexes. The Cr–O distances for the oxalate ligand (av. 2.00(1) Å) are slightly longer than those for the eddp ligand (av. 1.91(2) Å). Averaged distance between Cr···Nd is 5.876(2) Å, which is much longer than the Cr···M distances of the other oxalate-bridged complexes; [Cr(salen)(μ-ox)Cu(acpy)] (5.482(3) Å) (salen = *N, N'*-ethylenebis(salicylideneaminate), acpy = *N*-acetylacetonylidene-*N*-(2-pyridylethyl)aminate),[16] [CuCr$_2$(bpy)$_2$(μ-ox)$_2$(ox)$_2$(H$_2$O)$_2$]·H$_2$O (5.288 Å) (bpy = 2,2'-bipyridine),[15(a)] [CoCr$_2$(bpy)$_2$(μ-ox)$_2$(ox)$_2$(H$_2$O)$_2$]·1.5H$_2$O (5.288 Å),[15(b)] [MnCr$_2$(bpy)$_2$(μ-ox)$_4$]$_n$ (5.533–5.573 Å),[15(b)] and {[P(Ph)$_4$][MnCr(ox)$_3$]}$_n$ (5.42–5.45 Å).[11(d)] Many oxalate-

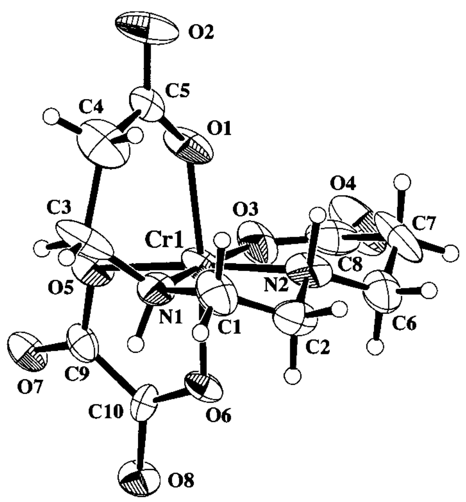

Figure 2. Structure of $[Cr(eddp)(ox)]^-$ unit (Cr1) with the Δ form.

bridged complexes are well known for their ability to transmit electronic effects between paramagnetic centers separated from each other by more than 5 Å.[13] Therefore, the present complex is expected to show new d–f interaction between paramagnetic Cr(III) and Nd(III) ions.

The absorption maxima of **1** are shifted to lower wavelength than those of the *unsym-cis*-$[Cr(eddp)(ox)]^-$.[20] The peak positions of the spectrum in solid state are almost the same as those in water. It reveals that **1** retains its tetranuclear structure even in water. Such a stability improves that this $[Cr(eddp)(ox)]^-$ unit is appropriate for the building block to create the Cr^{III}–Ln^{III} heteropolynuclear complexes. Infrared spectra show that two strong and well-separated bands (1712 and 1689 cm^{-1}) corresponding to the $\nu_{as}(COO^-)$ of oxalate for the $Na[Cr(eddp)(ox)]\cdot 3H_2O$ shift to lower wavenumber (1675 cm^{-1}) and are broadened for **1**. It reveals that the C–O bond of the oxalate ligand in the $[Cr(eddp)(ox)]^-$ are weakened by coordinating to the Nd ion.

Further study on the synthesis and some properties of a series of these oxalate-bridged Cr^{III}–Ln^{III} complexes is in progress.

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8 Elemental analysis: Calcd for $Nd\{Cr(eddp)(ox)\}_3\cdot 15H_2O$, C, 25.00; H, 5.03; N, 5.83%. Found: C, 25.06; H, 4.84; N, 5.74%.

9 Crystals are unstable in the air. The crystal was sealed into grass capillary during the data collection.

10 Crystal data for $[Nd\{Cr(eddp)(ox)\}_3(H_2O)_3]\cdot 12H_2O$ (**1**), $Cr_3NdC_{30}H_{48}N_6O_{27}\cdot 12H_2O$, F.W = 1441.16: Triclinic, $P\bar{1}$(#2), $Z = 2$, $a = 15.91(2)$, $b = 16.26(2)$, $c = 13.81(2)$ Å, $\alpha = 108.1(1)$, $\beta = 115.15(8)$, $\gamma = 70.78(10)°$, $V = 2992(7)$ Å^3, $D_{calcd} = 1.599$ gcm^{-3}, $\mu = 1.484$ mm^{-1} for MoKα radiation ($\lambda = 0.71069$ Å). Measurements were carried out on a Rigaku AFC7S diffractometer. The structure was solved by a direct method and refined by a full-matrix least-square. Final R = 0.109 and Rw = 0.140 for 3697 observed reflections ($I > 2.00\sigma(I)$).

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20 Absorption data (nm (ε / mol^{-1}dm^{3}cm^{-1})): 523.0 (124.8), 391.3 (75.8) for *unsym-cis*-$[Cr(eddp)(ox)]^-$; 520.0 (160.5), 389.3 (106.6) for **1** in H_2O.