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SCIENCE DIRECT

Polyhedron 22 (2003) 1455–1459

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Oxalato-bridged di- and trinuclear Co(III)–Dy(III) complexes derived from mononuclear Co(III) complex with nitrilotriacetate

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Received 6 January 2003; accepted 3 March 2003

Abstract

The divalent mononuclear complex anion, $[Co(nta)(ox)]^{2-}$ (nta = nitrilotriacetate, ox = oxalate) functions as an effective building-block for construction of the oxalato-bridged heteropolynuclear lanthanide(III) complexes, and reacts with Dy^{3+} ion by the molar ratio of 1:1 to form a novel dinuclear Co(III)–Dy(III) complex, $[Dy\{Co(nta)(\mu\text{-}ox)\}(H_2O)_7]^+$ (**1**). A similar reaction by the ratio of 2:1 results in the formation of trinuclear species, $[Dy\{Co(nta)(\mu\text{-}ox)\}_2(H_2O)_5]^-$ (**2**). The X-ray structural analyses for **1** and **2** revealed that each of the Dy(III) atoms in these complexes takes a nine-coordinated tricapped trigonal-prismatic geometry. The two characteristic bands for the Dy^{3+} ions in the diffuse reflectance spectra reflect differences in the coordination environments of Dy(III) atoms between **1** and **2**. Although no significant distinctions are recognized for the geometries of the Co(III) units between **1** and **2**, furthermore, the reflectance spectra indicate distinguishable electronic states of Co(III) atoms from each other.

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Keywords: Heteropolynuclear cobalt(III)–dysprosium(III) complexes; Oxalato-bridged complexes; Nitrilotriacetate complexes; X-ray structures; Diffuse reflectance spectra

1. Introduction

The heteropolynuclear complexes comprised of transition-metal and lanthanide ions are attracting great interest for their characteristic stereo- and physicochemical properties, and constructions of such complexes have been investigated from various approaches [1–9]. It has been shown that the mononuclear transition-metal complexes involving oxalate (ox) can function as effective building-blocks for constructions of such heteropolynuclear complexes, accompanied by the formations of oxalate-bridged structures with lanthanide(III) ions [5–9]. For instance, the reaction of $[Cr(eddp)(ox)]^-$ (eddp = ethylenediamine-*N*,*N*′-dipropionate) with Nd^{3+} ion gave an oxalato-bridged tetranuclear complex, $[Nd\{Cr(eddp)(\mu\text{-}ox)\}_3(H_2O)_3]$ [5]. On the other hand, the reaction of $[Cr(ox)_2(bpy)]^-$ (bpy = 2,2′-bipyridine) with Pr^{3+} ion yielded a hexanuclear complex, $[Pr_2(\mu\text{-}ox)\{Cr(bpy)(\mu\text{-}ox)(ox)\}_4(H_2O)_6]$ [6]. From the reaction of $[Cr(acac)_2(ox)]^-$ (acac = acetylacetonate) with Yb^{3+} ion ligated by hydrotris(pyrazol-1-yl)borate ($HBPz_3^-$), furthermore, a dinuclear complex, $[Yb(HBpz_3)_2\{Cr(acac)_2(\mu\text{-}ox)\}]$ was formed [7]. It can be regarded therefore that the generating oxalato-bridged heteropolynuclear structures are significantly affected by nature of the used mononuclear transition-metal complexes as well as the coordination surroundings around the lanthanide ions. Although several types of the complexes comprised of transition-metal and lanthanide ions were synthesized with the aid of such monovalent anionic building-blocks [5–9], the possibilities for incorporations of lanthanide ions into oxalato-bridged polynuclear structures by the uses of mononuclear transition-metal complexes other than the monovalent anionic species remain equivocal. In the present work, we have investigated the reactions of the divalent mononuclear complex anion, $[Co(nta)(ox)]^{2-}$ (nta = nitrilotriacetate), with Dy^{3+} ion by the ratios of 1:1, 2:1 and more than 3:1. As a result, the formations of oxalato-bridged di- and trinuclear complexes, $[Dy\{Co(nta)(\mu\text{-}ox)\}(H_2O)_7]^+$ (**1**) and [Dy{Co(nta)(μ-

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0277-5387/03/$ - see front matter © 2003 Elsevier Science Ltd. All rights reserved.
doi:10.1016/S0277-5387(03)00122-0

ox)}$_2$(H_2O)$_5$]$^-$ (**2**), were recognized for the ratios of 1:1 and more than 2:1, respectively. The diffuse reflectance spectral behaviors of these complexes are also discussed in relation to their X-ray crystal structures.

2. Experimental

2.1. Materials

$CoCl_2 \cdot 6H_2O$, $DyCl_3 \cdot 6H_2O$, oxalic acid (H_2ox), and nitrilotriacetic acid (H_3nta) were purchased from Wako Pure Chemical Ind. Co., Ltd, K_2[Co(nta)(ox)]$\cdot 2H_2O$ was prepared by modified method from the literature [10]. The other chemicals were obtained from Wako Pure Chemical Ind. Co., Ltd, Tokyo Chemical Co., Ltd, or Kanto Chemical Co., Inc. All of the chemicals were of reagent grade and used without further purification.

2.2. Preparations of the complexes

2.2.1. Synthesis of [Dy{Co(nta)(μ-ox)}(H_2O)$_7$]Cl (*1Cl*)

To a solution containing $DyCl_3 \cdot 6H_2O$ (0.38 g, 1.0 mmol) in 5 ml H_2O was added K_2[Co(nta)(ox)]$\cdot 2H_2O$ (0.45 g, 1.0 mmol). After the mixture was stirred at room temperature (r.t.) for 10 min, a saturated NaCl solution (5 ml) was added to the resulting violet solution. The whole was allowed to stand at 4 °C for several days. The resulting violet crystals of **1**Cl$\cdot 3H_2O$, in which a well-formed crystal was used for the X-ray structural analysis, were collected by filtration. Yield: 0.51 g (72% based on Co). *Anal*. Found: C, 13.48; H, 3.65; N, 1.89; Co, 8.10; Dy, 22.52%. Calc. for **1**Cl$\cdot 3H_2O$ = $C_8H_{26}NO_{20}ClCoDy$: C, 13.47; H, 3.67; N, 1.96; Co, 8.26; Dy, 22.78%. Diffuse reflectance spectrum: ν_{max} (10^3 cm^{-1}): 12.38, 13.18, 18.18, 25.38, 32.15.

2.2.2. Synthesis of K[Dy{Co(nta)(μ-ox)}$_2$(H_2O)$_5$] (*K2*)

To a solution containing $DyCl_3 \cdot 6H_2O$ (0.38 g, 1.0 mmol) in 5 ml H_2O was added 0.90 g (2.0 mmol) of K_2[Co(nta)(ox)]$\cdot 2H_2O$. After the mixture was stirred at r.t. for 10 min, the obtained violet solution was allowed to stand at 4 °C for several days. The resulting violet crystals of K**2**$\cdot 9H_2O$, in which a well-formed crystal was used for the X-ray structural analysis, were collected by filtration. Yield: 0.78 g (69% based on Co). *Anal*. Found: C, 17.12; H, 3.63; N, 2.42; Co, 10.44; Dy, 14.13%. Calc. for K**2**$\cdot 9H_2O$ = $C_{16}H_{40}N_2O_{34}KCo_2Dy$: C, 17.10; H, 3.59; N, 2.49; Co, 10.49; Dy, 14.26%. Diffuse reflectance spectrum: ν_{max} (10^3 cm^{-1}): 12.39, 13.23, 18.25, 25.32, 32.47.

2.3. Measurements

The diffuse reflectance spectra were recorded with a JASCO Ubest V-570 spectrophotometers equipped with an integrating sphere apparatus. The elemental analyses (C, H, and N) were performed by the Analysis Center of the University of Tsukuba. The concentrations of Co and Dy in the complexes were determined with a Nippon Jarrel-Ash ICPA-575 ICP spectrophotometer.

2.4. X-ray structure determination

Intensity data for **1**Cl$\cdot 3H_2O$ and K**2**$\cdot 9H_2O$ were collected on the Rigaku RASA-7S four-circle diffractometer with graphite-monochromatized Mo K_α radiation ($\lambda = 0.71069$ Å). The structures were solved by the direct method using SIR92 and refined by the full-matrix least-squares method using a TEXSAN program package [11]. All calculations were performed on an Indigo II computer. Crystal data for **1**Cl$\cdot 3H_2O$ = $C_8H_{26}NO_{20}$-ClCoDy, $F_W = 713.17$, monoclinic, space group $P2_1/n$ (no. 14), $a = 11.110(5)$, $b = 10.113(6)$, $c = 20.000(3)$ Å, $\beta = 100.95(2)°$, $V = 2206(1)$ Å^3, $Z = 4$, $D_{calc} = 2.147$ g cm^{-3}, $\mu = 4.332$ mm^{-1}, crystal size $0.15 \times 0.15 \times 0.15$ mm, trans. factors 0.92–1.00, 5306 reflections measured ($2\theta_{max} = 55.2°$), 2850 observed reflections [$I > 2.00\sigma(I)$] used in the refinement, $R = 0.054$, $R_w = 0.065$ and GOF = 1.49 for 289 parameters. Crystal data for K**2**$\cdot 9H_2O$ = $C_{16}H_{40}N_2O_{34}KCo_2Dy$, $F_W = 1123.95$, monoclinic, space group $P2_1/n$ (no. 14), $a = 11.434(4)$, $b = 10.289(4)$, $c = 32.793(4)$ Å, $\beta = 93.88(2)°$, $V = 3849(1)$ Å^3, $Z = 4$, $D_{calc} = 1.939$ g cm^{-3}, $\mu = 2.999$ mm^{-1}, crystal size $0.10 \times 0.10 \times 0.50$ mm, trans. factors 0.64–0.95, 9274 reflections measured ($2\theta_{max} = 55.0°$), 5263 observed reflections [$I > 2.00\sigma(I)$] used in the refinement, $R = 0.063$, $R_w = 0.077$ and GOF = 1.51 for 514 parameters.

3. Results and discussion

3.1. Syntheses

The divalent mononuclear complex anion, [Co(nta)(ox)]$^{2-}$ reacts with Dy^{3+} ion by the molar ratio of 1:1 to form a dinuclear complex, [Dy{Co(nta)(μ-ox)}(H_2O)$_7$]$^+$ (**1**). A similar reaction by the ratio of 2:1 resulted in the formation of the trinuclear complex, [Dy{Co(nta)(μ-ox)}$_2$(H_2O)$_5$]$^-$ (**2**). These imply that [Co(nta)(ox)]$^{2-}$ can function as an effective building-blocks for constructions of the oxalato-bridged hetero-polynuclear structures incorporated with lanthanide(III) ions. Although the formation of higher polynuclear species, such as [Dy{Co(nta)(μ-ox)}$_3$(H_2O)$_3$]$^{3-}$, was also expected for the reaction between [Co(nta)(ox)]$^{2-}$ and Dy^{3+} ion as in the case of the reaction between

$[Cr(eddp)(ox)]^-$ and Nd^{3+} ion [5], the reactions even at the ratio of $[Co(nta)(ox)]^{2-}$ and Dy^{3+} ion with more than 3:1 gave only the trinuclear species (**2**). This indicates that the generating heteropolynuclear species in such reactions are significantly dependent on nature of the used mononuclear transition-metal complexes as building-blocks. By using monovalent anionic mononuclear transition-metal complexes, such as $[Cr(eddp)(ox)]^-$, $[Cr(ox)_2(bpy)]^-$, and $[Cr(acac)_2(ox)]^-$, as building-blocks for the incorporations of lanthanide(III) ions into oxalato-bridged heteropolynuclear structures, on the other hand, only the neutral species are obtained [5–9]. This implies that neutralization of charge is one of the driving-forces for formations of such heteropolynuclear structures. In the reactions between $[Co(nta)(ox)]^{2-}$ and Dy^{3+} ion, it is noteworthy that only the relatively lower-charged species, monovalent anionic **1** and monovalent cationic **2**, can be isolated. Taking these facts into considerations, it is suggested that the electronic charges of the used mononuclear transition-metal complexes as building-blocks significantly affect the formations of oxalato-bridged heteropolynuclear complexes incorporated with lanthanide(III) ions.

3.2. Structures of complexes

The X-ray structural analyses revealed that $\mathbf{1}Cl\cdot 3H_2O$ is comprised of a monovalent complex cation, one chloride anion, and three H_2O molecules, and that $K\mathbf{2}\cdot 9H_2O$ contains a monovalent complex anion, one potassium cation, and nine H_2O molecules. The complex cation **1** involves one Co(III) atom and one Dy(II) atom to form a dinuclear structure, while the complex anion **2** contains two Co(III) atoms and one Dy(III) atom to generate a trinuclear structure. These are consistent with the results of the plasma emission spectral analyses, which gave the values of Co(III):Dy(III) = 1:1 for **1** and 2:1 for **2**. The Dy(III) atom in **1** is bridged by two O atoms from ox in the $[Co(nta)(ox)]^{2-}$ unit, and the remaining sites are occupied by seven O atoms of H_2O molecules to take a nine-coordinated geometry (Fig. 1). On the other hand, the Dy(III) atom in **2** is coordinated by four O atoms from the two $[Co(nta)(ox)]^{2-}$ units and five O atoms of H_2O molecules, forming a nine-coordination environment (Fig. 2). These nine-coordinated geometries around the Dy(III) atoms in **1** and **2** can be regarded as tricapped trigonal-prism. In **1**, namely, one bridging O atom in ox (O9) and two H_2O molecules (O16 and O17) are situated on the tricapped positions of the polyhedron, and another bridging O atom in ox (O10) and five H_2O molecules (O11, O12, O13, O14, and O15) are on the top and bottom of the trigonal-prism. In **2**, on the other hand, one of two bridging O atoms in each ox (O9 and O20) and one H_2O molecule (O25) are located on the tricapped positions, and the remaining bridging O atom in of each ox (O10 and O19) and four H_2O molecules (O21, O22, O23, and O24) are on the top and bottom of the trigonal-prism. It is noted that the Dy–O distances (av. 2.495(8) Å for **1**, 2.469(7) Å for **2**) responsible for the O atoms on the tricapped positions are considerably longer than those (av. 2.402(8) Å for **1**, 2.414(7) Å for **2**) on the trigonal-prism (Tables 1 and 2). A similar trend was also recognized for the geometry around the Nd(III) center in the oxalato-bridged tetranuclear complex, $[Nd\{Cr(eddp)(\mu\text{-}ox)\}_3(H_2O)_3]$ [5]. It seems therefore that these trends are characteristic for the nine-coordinated geometries of lanthanide ions in such types of oxalato-bridged polynuclear complexes. Each of the two $[Co(nta)(ox)]^{2-}$ units in **2** shows almost the same structure as that in **1**. Namely, the bond distances and angles around Co(III) atoms in **1** and **2** are essentially consistent with each other. Accordingly, there is no significant distinction in the geometries of the Co(III) units between **1** and **2**. Although a similar tetranuclear species, $[Dy\{Co(nta)(\mu\text{-}ox)\}_3(H_2O)_3]^{3-}$, to $[Nd\{Cr(eddp)(\mu\text{-}ox)\}_3(H_2O)_3]$, can be also regarded as possible from a structural point of view, on the other hand, the reactions even at the ratio of $[Co(nta)(ox)]^{2-}$ and Dy^{3+} ion with more than 3:1 gave only the trinuclear species (**2**). This seems to indicate that the electronic charges of the used mononuclear transition-metal complexes as

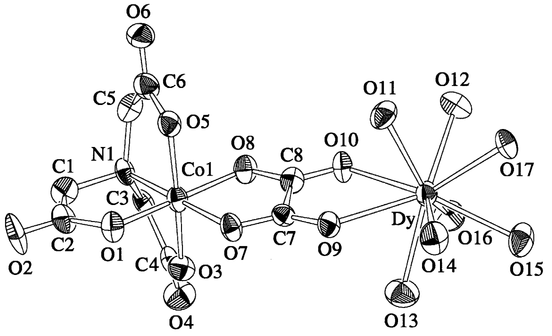

Fig. 1. Perspective view of $[Dy\{Co(nta)(ox)\}(H_2O)_7]^+$ (**1**) with the atomic labeling scheme (ellipsoids at 50% probability).

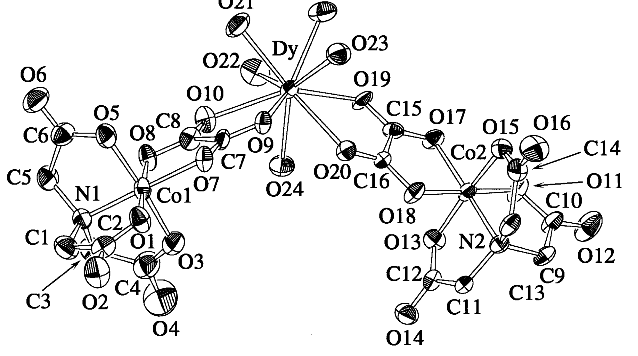

Fig. 2. Perspective view of $[Dy\{Co(nta)(ox)\}_2(H_2O)_5]^-$ (**2**) with the atomic labeling scheme (ellipsoids at 50% probability).

Table 1
Selected bond distances (Å) and angles (°) of [Dy{Co(nta)(μ-ox)}$(H_2O)_7$]Cl·$3H_2O$ (**1**Cl·$3H_2O$)

Bond distances			
Dy–O(9)	2.510(7)	Dy–O(10)	2.443(6)
Dy–O(11)	2.381(8)	Dy–O(12)	2.387(8)
Dy–O(13)	2.411(8)	Dy–O(14)	2.383(8)
Dy–O(15)	2.405(8)	Dy–O(16)	2.447(8)
Dy–O(17)	2.528(7)	Co(1)–O(1)	1.876(7)
Co(1)–O(3)	1.893(8)	Co(1)–O(5)	1.903(7)
Co(1)–O(7)	1.935(7)	Co(1)–O(8)	1.926(7)
Co(1)–N(1)	1.919(8)		
Bond angles			
O(9)–Dy–O(10)	65.6(2)	O(9)–Dy–O(11)	69.9(3)
O(9)–Dy–O(12)	130.9(3)	O(9)–Dy–O(13)	67.0(3)
O(9)–Dy–O(14)	67.2(2)	O(9)–Dy–O(15)	133.8(3)
O(9)–Dy–O(16)	118.8(2)	O(9)–Dy–O(17)	124.4(2)
O(10)–Dy–O(11)	77.9(3)	O(10)–Dy–O(12)	75.5(3)
O(10)–Dy–O(13)	85.9(3)	O(10)–Dy–O(14)	132.7(3)
O(10)–Dy–O(15)	140.9(3)	O(10)–Dy–O(16)	70.8(3)
O(10)–Dy–O(17)	139.4(2)	O(11)–Dy–O(12)	73.8(3)
O(11)–Dy–O(13)	136.9(3)	O(11)–Dy–O(14)	83.3(3)
O(11)–Dy–O(15)	136.7(3)	O(11)–Dy–O(16)	137.5(3)
O(11)–Dy–O(17)	71.6(3)	O(12)–Dy–O(13)	139.9(3)
O(12)–Dy–O(14)	138.8(3)	O(12)–Dy–O(15)	95.3(3)
O(12)–Dy–O(16)	71.1(3)	O(12)–Dy–O(17)	70.6(3)
O(13)–Dy–O(14)	78.9(3)	O(13)–Dy–O(15)	77.0(3)
O(13)–Dy–O(16)	69.2(3)	O(13)–Dy–O(17)	134.7(3)
O(14)–Dy–O(15)	78.4(3)	O(14)–Dy–O(16)	139.2(3)
O(14)–Dy–O(17)	69.8(3)	O(15)–Dy–O(16)	70.3(3)
O(15)–Dy–O(17)	65.3(3)	O(16)–Dy–O(17)	116.7(3)
O(1)–Co(1)–O(3)	91.9(3)	O(1)–Co(1)–O(5)	90.3(3)
O(1)–Co(1)–O(7)	91.8(3)	O(1)–Co(1)–O(8)	177.6(3)
O(1)–Co(1)–N(1)	88.8(3)	O(3)–Co(1)–O(5)	172.4(3)
O(3)–Co(1)–O(7)	93.6(3)	O(3)–Co(1)–O(8)	89.6(3)
O(3)–Co(1)–N(1)	85.4(3)	O(5)–Co(1)–O(7)	93.5(3)
O(5)–Co(1)–O(8)	88.4(3)	O(5)–Co(1)–N(1)	87.4(3)
O(7)–Co(1)–O(8)	86.3(3)	O(7)–Co(1)–N(1)	178.9(3)
O(8)–Co(1)–N(1)	93.1(3)		

building-blocks significantly affect the formations of oxalato-bridged heteropolynuclear complexes incorporated with lanthanide(III) ions.

3.3. Diffuse reflectance spectra

The diffuse reflectance spectrum of **1**Cl·$3H_2O$ exhibits five bands at 12.38, 13.18, 18.18, 25.38, and 32.15 × 10^3 cm^{-1} in the region of 12–40 × 10^3 cm^{-1}. Among these five bands, 18.18, 25.38, and 32.15 × 10^3 cm^{-1} ones are assigned as the transitions in the Co(III)NO_5 chromophore [11]. The remaining two bands at 12.38 and 13.18 × 10^3 cm^{-1} are characteristic for the Dy(III) species [12], and can be regarded as localized electronic transitions on the Dy(III) atom. The three intense bands due to the Co(III) unit correspond well with those observed for K_2[Co(nta)(ox)]$2H_2O$ [13], but are considerably shifted compared to the latter parent mononuclear Co(III) complex. This seems to reflect the formation of oxalato-bridged dinuclear structure of **1**.

Table 2
Selected bond distances (Å) and angles (°) of K[Dy{Co(nta)(μ-ox)}$_2(H_2O)_5$]·$9H_2O$ (**2**K·$9H_2O$)

Bond distances			
Dy–O(9)	2.478(6)	Dy–O(10)	2.460(6)
Dy–O(19)	2.425(6)	Dy–O(20)	2.493(6)
Dy–O(21)	2.414(7)	Dy–O(22)	2.375(7)
Dy–O(23)	2.378(7)	Dy–O(24)	2.434(7)
Dy–O(25)	2.435(7)	Co(1)–O(1)	1.860(7)
Co(1)–O(3)	1.880(7)	Co(1)–O(5)	1.887(7)
Co(1)–O(7)	1.931(6)	Co(1)–O(8)	1.923(7)
Co(1)–N(1)	1.906(8)	Co(2)–O(11)	1.868(6)
Co(2)–O(13)	1.881(6)	Co(2)–O(15)	1.884(7)
Co(2)–O(17)	1.933(6)	Co(2)–O(18)	1.912(6)
Co(2)–N(2)	1.911(7)		
Bond angles			
O(9)–Dy–O(10)	65.5(2)	O(9)–Dy–O(19)	132.5(2)
O(9)–Dy–O(20)	66.3(2)	O(9)–Dy–O(21)	78.3(2)
O(9)–Dy–O(22)	138.3(2)	O(9)–Dy–O(23)	71.8(2)
O(9)–Dy–O(24)	95.1(2)	O(9)–Dy–O(25)	135.2(2)
O(10)–Dy–O(19)	138.4(2)	O(10)–Dy–O(20)	110.8(2)
O(10)–Dy–O(21)	71.7(2)	O(10)–Dy–O(22)	73.0(2)
O(10)–Dy–O(23)	131.3(2)	O(10)–Dy–O(24)	68.7(2)
O(10)–Dy–O(25)	130.7(2)	O(19)–Dy–O(20)	66.4(2)
O(19)–Dy–O(21)	140.0(2)	O(19)–Dy–O(22)	82.4(2)
O(19)–Dy–O(23)	88.2(2)	O(19)–Dy–O(24)	72.2(2)
O(19)–Dy–O(25)	68.2(2)	O(20)–Dy–O(21)	137.6(2)
O(20)–Dy–O(22)	136.4(2)	O(20)–Dy–O(23)	69.5(2)
O(20)–Dy–O(24)	69.7(2)	O(20)–Dy–O(25)	118.5(2)
O(21)–Dy–O(22)	85.8(3)	O(21)–Dy–O(23)	78.0(2)
O(21)–Dy–O(24)	138.7(3)	O(21)–Dy–O(25)	71.9(3)
O(22)–Dy–O(23)	141.8(3)	O(22)–Dy–O(24)	72.2(3)
O(22)–Dy–O(25)	72.3(3)	O(23)–Dy–O(24)	139.0(3)
O(23)–Dy–O(25)	69.8(3)	O(24)–Dy–O(25)	129.3(3)
O(1)–Co(1)–O(3)	90.8(3)	O(1)–Co(1)–O(5)	91.7(3)
O(1)–Co(1)–O(7)	91.8(3)	O(1)–Co(1)–O(8)	177.8(3)
O(1)–Co(1)–N(1)	89.6(3)	O(3)–Co(1)–O(5)	174.0(3)
O(3)–Co(1)–O(7)	91.5(3)	O(3)–Co(1)–O(8)	88.1(3)
O(3)–Co(1)–N(1)	87.6(3)	O(5)–Co(1)–O(7)	93.9(3)
O(5)–Co(1)–O(8)	89.6(3)	O(5)–Co(1)–N(1)	87.0(3)
O(7)–Co(1)–O(8)	86.4(3)	O(7)–Co(1)–N(1)	178.4(3)
O(8)–Co(1)–N(1)	92.2(3)	O(11)–Co(2)–O(13)	90.9(3)
O(11)–Co(2)–O(15)	90.6(3)	O(11)–Co(2)–O(17)	91.8(3)
O(11)–Co(2)–O(18)	178.5(3)	O(11)–Co(2)–N(2)	89.6(3)
O(13)–Co(2)–O(15)	174.2(3)	O(13)–Co(2)–O(17)	92.6(3)
O(13)–Co(2)–O(18)	88.8(3)	O(13)–Co(2)–N(2)	86.9(3)
O(15)–Co(2)–O(17)	93.0(3)	O(15)–Co(2)–O(18)	89.8(3)
O(15)–Co(2)–N(2)	87.5(3)	O(17)–Co(2)–O(18)	86.8(3)
O(17)–Co(2)–N(2)	178.6(3)	O(18)–Co(2)–N(2)	91.9(3)

Similarly to the case of **1**Cl·$3H_2O$, K**2**·$9H_2O$ shows three bands due to the Co(III)NO_5 chromophore at 18.25, 25.32, and 32.47 × 10^3 cm^{-1}, and two characteristic bands for the Dy(III) atom at 12.39, 13.23 × 10^3 cm^{-1}. However, all the five bands of K**2**·$9H_2O$ are slightly shifted compared with the corresponding bands of **1**Cl·$3H_2O$. This implies that the electronic states of Co(III) and Dy(III) atoms in **2** are rather different from those in **1**, in spite of almost the same geometries around Co(III) units in **1** and **2** as each other (Figs. 1 and 2).

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 200084 and 200085 for **1**Cl·3H_2O and K**2**·9H_2O, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

This work was partially supported by a Grant-in-Aid for Scientific Research No. 14540510 from the Ministry of Education, Science, Sports, and Culture.

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