研究简报

一个二核钒配合物的合成及晶体结构：$NH_4[(V^{IV}O)_2(\mu_2\text{-}O)(nta)_2][Eu^{III}(H_2O)_9]$

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Synthesis and Crystal Structure of a Binuclear Vanadium Complex: $NH_4[(V^{IV}O)_2(\mu_2\text{-}O)(nta)_2][Eu^{III}(H_2O)_9]$

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Abstract: A binuclear vanadium complex $NH_4[(V^{IV}O)_2(\mu_2\text{-}O)(nta)_2][Eu^{III}(H_2O)_9]$ was synthesized by reaction of NH_3VO_3, nitrilotriacetic acid and $EuCl_3$ in one aqueous solution. The crystal X-ray analysis shows that the complex contains one binuclear vanadium anion $[(V^{IV}O)_2(\mu_2\text{-}O)(nta)_2]^{4-}$ and one $[Eu^{III}(H_2O)_9]^{3+}$ cation. The molecules are built up to a three-dimensional supramolecular structure through hydrogen bonding. CCDC: 238716.

Key words: nitrilotriacetic acid; vanadium; synthesis and crystal structure

0 Introduction

Contemporary interest in the coordination chemistry of oxovanadium(Ⅳ), oxovanadium(Ⅴ) and dioxovanadium(Ⅴ) derives from their important biological and medicinal applications[1~3]. Recently, the inorganic-organic hybrid materials based on vanadium oxides have attracted much attention[4~8]. Therefore, the discovery of new vanadium oxide complexes and the rational design of such solid materials remain an important and very active subject. As a part of our investigation on the vanadium complexes, we herein present the synthesis and crystal structure of a binuclear vanadium complex $NH_4[(V^{IV}O)_2(\mu_2\text{-}O)(nta)_2][Eu^{III}(H_2O)_9]$ (**1**) (H_3nta=nitrilotriacetic acid).

1 Experimental

1.1 Synthesis of 1

A mixture of NH_4VO_3 (0.15 g, 1.28 mmol), H_3nta (1.36 g, 7.12 mmol), $EuCl_3$ (0.32 g, 1.24 mmol) and H_2O (25 mL) was heated to boil till NH_4VO_3 being dissolved completely. The deep blue solution was allowed to stand at room temperature without further disturbing for about five days to give deep blue crystals. Anal. Calcd. for $C_{12}H_{34}N_3O_{24}EuV_2$(%): C, 16.78; H, 3.96; N, 4.89. Found(%): C, 16.71; H, 3.89; N,

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4.78. IR (KBr pellet, cm^{-1}): 3 342(s), 1 612(s), 1 404(s), 1 277(w), 1 219(w), 1 126(w), 957(s), 916(s), 737(w), 623(w).

1.2 X-ray crystallography

A deep blue single crystal with dimensions of 0.32 mm × 0.21 mm × 0.09 mm was mounted on a computer-controlled Siemens SMART CCD diffractometer equipped with graphite monochromated Mo$K\alpha$ radiation (λ=0.071 073 nm) at room temperature. Cell parameters were determined by the least-squares calculations with θ angles ranging from 1.75° to 25.10°. A total of 4 084 independent reflections were collected, giving 2 243 observed reflections with $I>2\sigma(I)$. Empirical absorption correction was applied through SADABS procedure. The structure was solved by a heavy atom method and refined on F^2 by full-matrix least-square using the SHELXTL-97 program package giving a final R_1=0.035 2, wR_2=0.091 8. The largest peak and hole on the final difference-Fourier map were 849 and −1 172 e·nm^{-3}, respectively. All non-hydrogen atoms were refined anistropically. All hydrogen atoms based on C atoms were generated from the difference Fourier map and refined with isotropic thermal parameters, while other hydrogen atoms were not located. Crystal data and structure refinement parameters are listed in Table 1, and selected bond lengths and angles are given in Table 2.

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2 Results and discussion

As shown in Fig.1, compound **1** contains one binuclear vanadium anion $[(V^{IV}O)_2(\mu_2\text{-}O)(nta)_2]^{4-}$, one $Eu(H_2O)_9^{3+}$ cation and one free ammonium ion. The binuclear anion has the similar structure to that of the previously reported vanadium anions [9~11], which is formed by an oxygen atom (μ_2-O) bridging two mononuclear vanadium anions $[(V^{IV}O)(nta)]^-$. The two anions $[(V^{IV}O)(nta)]^-$ are centrosymmetric via O8 atom (μ_2-O) locating on the special position (3/4, 3/4, 0). Each vanadium atom in the mononuclear anion is in octahedral coordination environment. The distorted octahedron is defined by one vanadyl oxygen atom (O7), one bridging oxygen atom (O8), three carboxyl oxygen atoms (O1, O3 and O5) and one nitrogen atom from the nta ligand, of which the basal plane is formed by O1, O3, O5 and O8 atoms with the mean deviation of 0.011 05 nm, while the apical positions are occupied by one vanadyl oxygen atom (O7) and one nitrogen atom, respectively. The V-O distances can be divided into three groups: (a) The V=O bond length is 0.160 7(4) nm, which is in the normal range of 0.156~0.163 nm for V^{IV}=O bond length[12]; (b) The V-O μ_2 bond length

Table 1 Crystal data and structure refinement for complex 1

Molecule formula	$C_{12}H_{34}EuN_3O_{24}V_2$
Molecule weight	858.26
Crystal size	0.32 × 0.21 × 0.09
Crystal color	Deep blue
Crystal system	Monoclinic
Space group	*C*2/*c*
a / nm	2.333 10(4)
b / nm	1.096 30(4)
c / nm	1.083 48(4)
β / (°)	92.77
V / nm^3	2.768 06(15)
Z	4
D_c / (g·cm^{-3})	2.059
F(000)	1712
Goodness of fit on F^2	1.101
Absorption coefficient / mm^{-1}	3.005
Largest diff. peak and hole / (e·nm^{-3})	849 / −1 172
Data / restraints / parameters	2 400 / 0 / 218
Final *R* indices [$I>2\sigma(I)$][a]	R_1= 0.035 2, wR_2= 0.091 8
R indices (all data)	R_1= 0.039 4, wR_2= 0.095 8

[a] $R_1=\sum(|F_o|-|F_c|)/\sum|F_0|$; $wR_2=[\sum w(F_o^2-F_c^2)^2/\sum w(F_o^2)^2]^{0.5}$

Table 2 Selected bond lengths (nm) and angles (°) for complex 1

V(1)-O(7)	0.160 7(4)	Eu(1)-O(10)	0.242 5(4)
V(1)-O(8)	0.180 23(8)	Eu(1)-O(12)	0.243 7(4)
V(1)-O(3)	0.198 9(4)	Eu(1)-O(11)	0.244 6(6)
V(1)-O(1)	0.201 0(4)	Eu(1)-O(9)	0.249 4(4)
V(1)-O(5)	0.206 6(4)	Eu(1)-O(13)	0.251 7(4)
V(1)-N(1)	0.229 2(4)		
O(7)-V(1)-O(8)	103.75(14)	O(3)-V(1)-O(5)	88.83(16)
O(7)-V(1)-O(3)	103.96(18)	O(1)-V(1)-O(5)	83.37(16)
O(8)-V(1)-O(3)	89.63(11)	O(7)-V(1)-N(1)	167.73(18)
O(7)-V(1)-O(1)	103.28(18)	O(8)-V(1)-N(1)	88.51(12)
O(8)-V(1)-O(1)	90.74(12)	O(3)-V(1)-N(1)	75.30(15)
O(3)-V(1)-O(1)	151.85(15)	O(1)-V(1)-N(1)	76.57(15)
O(7)-V(1)-O(5)	91.72(17)	O(5)-V(1)-N(1)	76.05(15)
O(8)-V(1)-O(5)	164.36(11)		

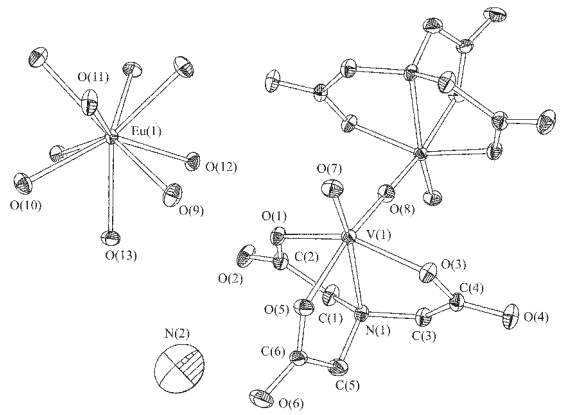

Fig.1　Molecule structure of **1**

All hydrogen atoms are omitted for clarity.

is 0.180 23(8) nm, showing partial multiple bond character; (c) The V-O_{nta} bond distances are 0.198 9(4), 0.201 0(4) and 0.206 6(4) nm, respectively. The V-N distance is 0.229 2(4) nm, which is slight longer than that in other vanadium nta complexes[9~11,13~15]. The Eu^{III} ion is 9-coordinated by water molecules with the Eu-O distances in the range of 0.242 5(4)~0.251 7(4) nm.

A remarkable feature of **1** is that there exists hydrogen bonding between the coordinated water molecules and the binuclear vanadium anions. The coordinated water molecules not only link up the adjacent binuclear vanadium anions to two-dimensional layer structure, but connect the two-dimensional layers into a three-dimensional framework through hydrogen bonding (Fig.2). The distances between the coordinated water molecules and the oxygen atoms of binuclear vanadium anions are in 0.271 4~0.308 6 nm range. However, no hydrogen bonding is involved between the ammonium cation and the binuclear vanadium anion.

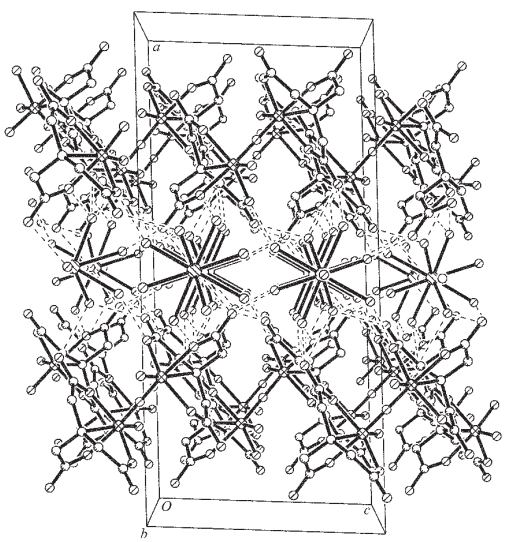

Fig.2　Three-dimensional structure of **1**

All hydrogen atoms are omitted for clarity.

The TG analysis is performed in the temperature range of 30~600 ℃, showing three steps weight losses (Fig.3). The first two steps occur in the range of 80~290 ℃, corresponding to the removal of NH_3 and coordinated water molecules. The weight loss is 20.53%, which is in accordance with the predicted value (calc. 20.97%). The last one step occurs in the range of 290~550 ℃, corresponding to the departure of organic ligand (Calcd. 43.81% weight loss). However, the observed weight loss (33.86%) is lower than the predicted value. This might be due to the retention of some carbonaceous residue in the final solid phase (black in color).

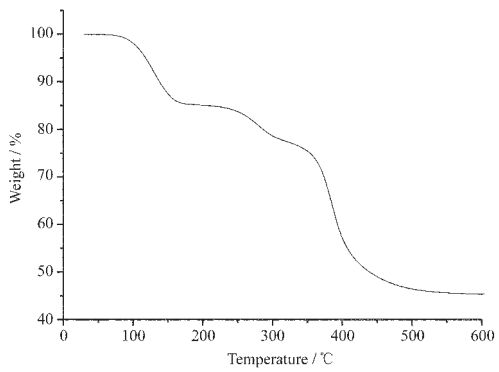

Fig.3　TG curve of **1**

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