ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2014, Vol. 40, No. 9, pp. 686–694. © Pleiades Publishing, Ltd., 2014.

Synthesis and Structural Characterization of Binuclear Ytterbium(III) Complexes with 2-Amino and 3-Amino Benzoic Acid[1]

S. Hussain[a, *], I. U. Khan[a], M. Akkurt[b], S. Ahmad[c], and M. N. Tahir[d]
[a] *Materials Chemistry Laboratory, Department of Chemistry, GC University, Lahore, 54000 Pakistan*
[b] *Department of Physics, Faculty of Sciences, Erciyes University, Kayseri, 38039 Turkey*
[c] *Department of Chemistry, University of Engineering and Technology, Lahore, 54890 Pakistan*
[d] *Department of Physics, University of Sargodha, Sargodha, Pakistan*
**e-mail: sajjaduet07@yahoo.com*

Received February 2, 2014

Abstract—Two novel homobinuclear ytterbium(III) complexes, $[Yb_2(2AMB)_6(H_2O)_4] \cdot 2C_2H_6O$ (**I**) and $Yb_2(3AMB)_6(H_2O)_4] \cdot 3H_2O$ (**II**) (2AMB = 2-aminobenzoic acid, 3AMB = 3-aminobenzoic acid) have been synthesized and characterized by elemental analysis, infrared spectroscopy, thermogravimetric analysis and X-ray crystallography (CIF files CCDC nos. 950103 (**I**), 921652 (**II**)). Complex **I** crystallizes in triclinic space group $P\bar{1}$ and complex **II** crystallizes in monoclinic space group $P2_1/n$. X-ray analysis shows that both complexes (**I**, **II**) have the dinuclear structure. The central Yb^{3+} ions in both complexes are eight-coordinated adopting distorted YbO_8 dodecahedral geometry. Each Yb^{3+} ion is coordinated to two O atoms from bridging carboxylate, four O atoms from the chelating carboxylate ligands and two O atoms of water molecules. The crystal structure of **I** and **II** are stabilized by N–H···O, O–H···O, O–H···N, and C–H···O hydrogen bonds, C–H···π interactions and weak π–π stacking interactions.

DOI: 10.1134/S107032841409005X

INTRODUCTION

Lanthanide complexes are of great interest because of their potential applications in the area of catalysis [1, 2], photochemistry [3, 4], contrast agents [5], ion exchange, superamolecular chemistry [6, 7], luminescence [8], pharmcacological [9] and diagnostic agents [10, 11].

Lanthanide complexes with carboxylic acids have been studied extensively because of their fascinating structural features and potential application in numbers of areas [12–14]. It has been seen that when aromatic carboxylic acids are used as ligands, lanthanide ions show higher luminescent stability than posses other ligand [4, 15]. The delocalized π-electrons act as strong absorbing chromophores and carboxylic group actively connects with oxophilic lanthanide cations [8, 16, 17]. Crystal structures of lanthanide complexes of several carboxylate ligands have been reported in recent years [18–22] which indicate that their dimensional diversity is controlled by lanthanide contraction [23].

On the basis of above mentioned facts, in the present study, we have synthesized trivalent complexes of ytterbium with 2-amino and 3-amino benzoic acid (2AMB and 3AMB). These complexes were investigated by means of elemental analysis, infrared spectroscopy, thermogravimetry, differential scanning colorimetry (TG–DSC) and X-ray crystallograhpy. The results provide important information about their structural features and thermal stability.

EXPERIMENTAL

Materials and measurements. $YbCl_3 \cdot 6H_2O$ was obtained from Alfa Aesar, a Johnson Matthey Company, Germany, 2-amino and 3-amino benzoic acids were obtained from Merck Chemical Co., Germany. The IR spectra of the complexes were recorded on a Perkin Elmer FTIR 180 spectrophotometer using KBr pellets over the frequency range 4000–400 cm^{-1}. Elemental analysis for C, H, and N were performed on a Varion Micro Cube, Elementar, Germany. Thermal analysis (25–1200°C) was recorded under a continuous nitrogen flow with a ramp rate of 10°C per minute using a Differential Scanning Calorimeter/Thermogravimeter Analyzer model SDT Q 600, TA Instruments, USA. Alumina crucibles were used for recording the TG–DSC curves.

Synthesis of complex I. 0.206 g (1.5 mmol) of 2AMB was dissolved in 15 mL ethanol and 8 drops of 1 M NaOH were added to this solution to raise the pH 6.5. $YbCl_3 \cdot 6H_2O$ (0.194 g, 0.5 mmol) was separately dissolved in 5 mL distilled water. The 2AMB solution was slowly added into $YbCl_3 \cdot 6H_2O$ solution.

---

[1] The article is published in the original.

After contunous stirring for one hour at room temperature, the solution was filtered and kept at room temperature for crystallization. After one week brown crystals appeared in the solution seperated by decantation (the yield was 43%, mp = 185°C).

For $[Yb_2(C_7H_6NO_2)_6(H_2O)_4] \cdot 2C_2H_6O$

anal. calcd., %:	C, 39.13;	H, 3.90;	N, 6.65.
Found, %:	C, 39.04;	H, 3.39;	N, 6.61.

Synthesis of complex II. 0.274 g (2 mmol) of 3AMB was dissolved in 15 mL ethanol and 9 drops of 1 M NaOH solution were added to lower the pH 6. $YbCl_3 \cdot 6H_2O$ (0.194 g, 0.5 mmol) was dissolved separately in distilled water. Both solutions were mixed and the reaction mixture was stirred for one hour at room temperature. The solution was filtered and kept at room temperature for crystallization. After about one week, brown crystals were appeared in the solution. These crystals were rinsed with ethanol and dried at filter paper (the yield was 48%, mp > 300°C).

For $[Yb_2(C_7H_6NO_2)_6(H_2O)_4] \cdot 3H_2O$

anal. calcd., %:	C, 41.63;	H, 4.24;	N, 6.33.
Found, %:	C, 41.57;	H, 4.02;	N, 6.45.

X-ray crystallography. Intensities for complexes I and **II** were recorded at room temperature on a Bruker Smart CCD diffractometer using graphite-monochromated MoK_α radiation ($\lambda = 0.71073$ Å). The crystal structures of complexes **I** and **II** were solved by direct methods with the program SHELXS-97 [24] and refined by the full-matrix least-squares technique on F^2 with the program SHELXL-97 [24]. The molecular structure plots were drawn by ORTEP 3 for Windows [25].

For complex **I** the aromatic C-bound H atoms were geometrically located and refined as riding with C–H = 0.93 Å and $U_{iso}(H) = 1.2 \times U_{eq}(C)$. The H atoms of the NH groups and water molecules were found from difference Fourier maps (N–H = 0.85(6)–0.87(6), O–H = 0.82(4)–0.84(4) Å) and their isotropic atomic displacement parameters were fixed to 1.2 (for N) or 1.5 (for O) × U_{eq} of the parent atom. The atoms of two ethanol solvent molecules which are symmetry related are disordered over two positions with occupancies of 0.505(6) and 0.495(6), respectively. They were isotropically refined by the atomic displacement parameter fixed to 0.05 $Å_2$.

For complex **II**, the atoms of the two aniline groups (with N(2) and N(6) are disordered over two sites with the refined occupancy ratios of 0.575(13) : 0.425(13) and 0.651(10) : 0.349(10), respectively. H atoms bounded to N and O atoms were located in difference Fourier maps and were refined with the distance restraints of N–H 0.90(2) and H···H 1.50(2) Å for NH_2 and O–H 0.85(1), H···H 1.287(2) Å for water molecules; their temperature factors were restrained to 1.5 times U_{eq}(N,O). Carbon bound H atoms were positioned geometrically and refined by using a riding model with C–H 0.93 and U_{iso}(H) 1.2 U_{eq}(C). The highest residual electron density peaks are located within 0.07 Å from atom C(16) and the deepest hole is located 0.07 Å from N(3). Omitted from the refinement were several reflections affected by the beam-stop: (0 0 2), (0 1 1), (–3 2 5), (–3 2 10), (0 2 2), (3 4 6), (0 4 9), (–3 4 10), (2 4 15), (5 4 14), (4 2 8), (1 2 11), and (–4 4 1). A summary of the crystallographic data and structure refinement of **I** and **II** are given in Table 1, selected bond lengths and bond angles are listed in Table 2.

Supplementary material for structures **I** and **II** has been deposited with the Cambridge Crystallographic Data Centre (nos. 950103 (**I**), 921652 (**II**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

IR spectra of **I** and **II** differ from those of free ligands, indicating that the ligands are coordinated to a metal atom. The main effect of coordination is observed on the frequency of carboxyl group.

For complex **I** the intense vibrations located at 1579 and 1453 cm^{-1} correspond to the symmetric and asymmetric stretching vibrations of carboxylate group. In complex **II**, these vibrations appear around 1560 and 1411 cm^{-1}, respectively. The shifts in frequencies indicate that the oxygen atoms of the carboxylic groups are coordinated to the metal ion [26–29]. There is no strong peak at frequency 1730–1690 cm^{-1} which indicates that no protonated oxygen atoms are present in both of these complexes as it is obvious from crystal structure [27]. The broad peak in frequency range 3500–3100 cm^{-1} is due to vibration of water which suggests the presence of water molecules in both these complexes [27, 30, 31]. The intense bands in the low frequency region 420–400 cm^{-1} are attributed due to metal oxygen bond vibrations [32].

Thermal stability of both complexes was investigated by thermal gravimetric analysis. The crystals of complex **I** undergo a rapid weight loss of 11.2% in the temperature range 60–125°C. It corresponds to four coordinated water molecules and two solvent molecules [33] (calcd. 12.37%). After removal of water and solvent molecules, complex **I** becomes stable and there is no chemical decomposition up to 310°C. As the temperature rises above 310°C, the subsequent complex decomposes slowly into two steps. At first step, the weight loss of 41.3% from 310 to 650°C corresponds to the decomposition of four ligands molecules (calcd. 41.04%). In the second step of decomposition, the weight loss of 19.7% between temperature range 775 to 1150°C attributes to the loss of remaining two carboxylate molecules of ligands. The total mass loss up to 1150°C is 72.08% that is in good agreement with

Table 1. Crystallographic data and structure refinement for **I** and **II**

Parameter	Value	
	I	**II**
Formula weight	1327.05	1288.96
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$
a, Å	9.1602(2)	11.1454(2)
b, Å	11.7706(3)	17.6661(4)
c, Å	12.866(3)	24.9218(5)
α, deg	96.617(1)	90
β, deg	94.794(1)	97.548(1)
γ, deg	112.197(1)	90
v, Å^3	1263.62(5)	4864.48(17)
Z	1	4
Temperture, K	293	293
ρ_{calcd}, g cm^{-3}	1.744	1.76
θ Range for data collection, deg	1.61–28.37	1.92–28.33
Crystal color	Brown	Brown
Crystal shape	Block	Block
Crystal size, mm	0.18 × 0.15 × 0.12	0.16 × 0.12 × 0.13
μ, mm^{-1}	3.76	3.90
T_{min}, T_{max}	0.5257, 0.7455	0.5256, 0.7462
Measured reflections	22821	47152
Independent reflections, R_{int}	6268 (0.026)	12009 (0.047)
Reflection with $I > 2\sigma(I)$	4097	9513
S	1.17	1.01
R, $wR(F^2)$	0.035, 0.107	0.041, 0.097
Parameters	347	600
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^{-3}	1.48/–3.32	2.23/–2.71

the calculated weight loss of 73.92% leaving Yb_2O_3 as residue.

For complex **II**, the first weight loss of 8.80% in the temperature range 60–120°C corresponds to the release of four coordinated and two uncoordinated water molecules [34] (calcd. 9.78%). After dehydration, the decomposition of the complex takes place in consecutive overlapping step. The second weight loss of 9.2% between 160 to 270°C corresponds to the release of one molecule of ligand (calcd. 10.56%). Third weight loss of 29% between temperature range 400 to 675°C is attributed to the release of three ligands molecules (calcd. 31.5%). Until 1200°C the total weight loss is 58% while decomposition process is still continuing.

DSC curves of both complexes **I** and **II** support the TGA analysis. The small endothermic peaks for **I** and **II** appear at about 100°C exhibit the dehydration step. The most prominent endothermic peaks appear at 875°C in both complexes **I** and **II** may indicate decomposition of ligands.

The molecular structure of **I** is shown in Fig. 1. The structure **I** of consists of homobinuclear $[Yb_2(C_7H_6NO_2)_6(H_2O)_4] \cdot 2C_6H_5OH$ molecules. Each Yb atom in the binulear complex adopts a distorted dodecahedral coordination geometry and is coordinated by two O atoms from water molecules and six O atom from 2-AMB molecules (two from bidentate bridging carboxylate and four from bidentate chelating carboxylate). The Yb–O bond lengths range from 2.193(4) to 2.431(4) Å with an average value of 2.324 Å which is comparable to that in other similar eight coordinated Yb(III) complexes [35]. The two water oxygen atoms have an average bond length 2.325 Å. The longest Yb---O bond distances are from the bidentate chelating carboxylate oxygen of (Yb(1)–

Table 2. Selected bond lengths (Å) and angles (deg) for **I** and **II***

Bond	*d*, Å	Bond	*d*, Å
		I	
Yb(1)–O(1)	2.419 (4)	O(3)–C(14)	1.273 (6)
Yb(1)–O(2)	2.331 (5)	O(4)–C(14)	1.271 (6)
Yb(1)–O(3)	2.431 (4)	O(6)–C(21)^{i}	1.242 (6)
Yb(1)–O(4)	2.335 (3)	O(8)–C(21)	1.251 (7)
Yb(1)–O(5)	2.312 (4)	O(9B)–C(23*B*)	1.501 (15)
Yb(1)–O(6)	2.193 (4)	O(9A)–C(23*A*)	1.456 (14)
Yb(1)–O(7)	2.338 (5)	N(1)–C(1)	1.366 (9)
Yb(1)–O(8)	2.236 (4)	N(2)–C(8)	1.362 (8)
O(1)–C(7)	1.264 (7)	N(3)–C(15)	1.370 (9)
O(2)–C(7)	1.271 (6)		
		II	
Yb(1)–O(6)	2.232 (3)	Yb(2)–O(1)	2.375 (4)
Yb(1)–O(9)	2.414 (4)	Yb(2)–O(2)	2.355 (4)
Yb(1)–O(10)	2.364 (4)	Yb(2)–O(3)	2.376 (4)
Yb(1)–O(11)	2.398 (4)	Yb(2)–O(4)	2.371 (5)
Yb(1)–O(12)	2.396 (3)	Yb(2)–O(5)	2.219 (4)
Yb(1)–O(13)	2.207 (4)	Yb(2)–O(7)	2.330 (4)
Yb(1)–O(15)	2.302 (5)	Yb(2)–O(8)	2.320 (3)
Yb(1)–O(16)	2.285 (5)	Yb(2)–O(14)	2.267 (3)
Angle	ω, deg	Angle	ω, deg
		I	
O(1)Yb(1)O(2)	54.58(14)	O(5)Yb(1)O(6)	80.14(17)
O(1)Yb(1)O(3)	111.85(13)	O(5)Yb(1)O(7)	149.70(17)
O(1)Yb(1)O(4)	83.71(12)	O(5)Yb(1)O(8)	80.83(17)
O(1)Yb(1)O(5)	121.85(15)	O(5)Yb(1)C(7)	97.39(16)
O(1)Yb(1)O(6)	154.90(15)	O(5)Yb(1)C(14)	102.91(15)
O(1)Yb(1)O(7)	76.53(15)	O(6)Yb(1)O(7)	78.47 (17)
O(1)Yb(1)O(8)	77.85(14)	O(6)Yb(1)O(8)	95.70 (16)
O(1)Yb(1)C(7)	27.27(14)	O(6)Yb(1)C(7)	177.52 (15)
O(1)Yb(1)C(14)	100.43(13)	O(6)Yb(1)C(14)	84.44 (15)
O(2)Yb(1)O(3)	79.51(14)	O(7)Yb(1)O(8)	80.21 (17)
O(2)Yb(1)O(4)	98.67(15)	O(7)Yb(1)C(7)	103.77 (16)
O(2)Yb(1)O(5)	72.35(16)	O(7)Yb(1)C(14)	96.12 (15)
O(2)Yb(1)O(6)	150.46(16)	O(8)Yb(1)C(7)	83.72 (16)
O(2)Yb(1)O(7)	131.07(16)	O(8)Yb(1)C(14)	176.21 (15)
O(2)Yb(1)O(8)	90.45(16)	C(7)Yb(1)C(14)	96.30 (15)
O(2)Yb(1)C(7)	27.31(15)	Yb(1)O(1)C(7)	91.5 (3)
O(2)Yb(1)C(14)	91.27(15)	Yb(1)O(2)C(7)	95.4 (4)
O(3)Yb(1)O(4)	54.02(12)	Yb(1)O(3)C(14)	91.9 (3)
O(3)Yb(1)O(5)	75.97(15)	Yb(1)O(4)C(14)	96.5 (3)
O(3)Yb(1)O(6)	83.64(15)	Yb(1)O(6)C(21)^{i}	173.9 (4)
O(3)Yb(1)O(7)	122.24(15)	Yb(1)O(8)C(21)	140.3(3)
O(3)Yb(1)O(8)	156.57(14)	N(1)C(1)C(2)	119.3(7)

Table 2. (Contd.)

Angle	ω, deg	Angle	ω, deg
O(3)Yb(1)C(7)	95.93(15)	N(1)C(1)C(6)	123.1 (6)
O(3)Yb(1)C(14)	27.23(12)	Yb(1)C(7)O(2)	57.3 (3)
O(4)Yb(1)O(5)	129.90(15)	Yb(1)C(7)C(6)	177.3 (4)
O(4)Yb(1)O(6)	90.66(15)	Yb(1)C(7)O(1)	61.3 (3)
O(4)Yb(1)O(7)	71.65(15)	Yb(1)C(14)C(13)	170.6(4)
O(4)Yb(1)O(8)	149.27(15)	Yb(1)C(14)O(3)	60.9 (3)
O(4)Yb(1)C(7)	91.05(14)	Yb(1)C(14)O(4)	56.5 (2)
O(4)Yb(1)C(14)	26.99(13)		
II			
O(6)Yb(1)O(9)	76.21(13)	O(1)Yb(2)O(2)	55.16 (12)
O(6)Yb(1)O(10)	84.83 (13)	O(1)Yb(2)O(3)	102.10 (13)
O(6)Yb(1)O(11)	134.60 (12)	O(1)Yb(2)O(4)	83.16 (15)
O(6)Yb(1)O(12)	80.50 (12)	O(1)Yb(2)O(5)	158.28 (14)
O(6)Yb(1)O(13)	92.10 (13)	O(1)Yb(2)O(7)	77.24 (13)
O(6)Yb(1)O(15)	152.53 (15)	O(1)Yb(2)O(8)	127.50 (13)
O(6)Yb(1)O(16)	82.30 (14)	O(1)Yb(2)O(14)	85.54 (13)
O(9)Yb(1)O(10)	54.35 (12)	O(2)Yb(2)O(3)	79.25 (13)
O(9)Yb(1)O(11)	123.85 (12)	O(2)Yb(2)O(4)	108.93 (16)
O(9)Yb(1)O(12)	124.09 (12)	O(2)Yb(2)O(5)	145.90 (14)
O(9)Yb(1)O(13)	149.45 (12)	O(2)Yb(2)O(7)	130.83 (13)
O(9)Yb(1)O(15)	81.17 (15)	O(2)Yb(2)O(8)	74.22 (12)
O(9)Yb(1)O(16)	73.94 (13)	O(2)Yb(2)O(14)	86.48 (13)
O(10)Yb(1)O(11)	79.53 (13)	O(3)Yb(2)O(4)	54.33 (15)
O(10)Yb(1)O(12)	73.64 (12)	O(3)Yb(2)O(5)	82.65 (13)
O(10)Yb(1)O(13)	153.90 (12)	O(3)Yb(2)O(7)	126.83 (15)
O(10)Yb(1)O(15)	94.57 (15)	O(3)Yb(2)O(8)	79.10 (14)
O(10)Yb(1)O(16)	128.29 (13)	O(3)Yb(2)O(14)	155.42 (13)
O(11)Yb(1)O(12)	54.25 (12)	O(4)Yb(2)O(5)	82.62 (16)
O(11)Yb(1)O(13)	84.43 (13)	O(4)Yb(2)O(7)	73.18 (16)
O(11)Yb(1)O(15)	71.65 (14)	O(4)Yb(2)O(8)	130.20 (15)
O(11)Yb(1)O(16)	139.37 (15)	O(4)Yb(2)O(14)	150.24 (14)
O(12)Yb(1)O(13)	80.29 (12)	O(5)Yb(2)O(7)	82.97 (15)

* Symmetry codes: ^{i} $1 - x, -y, 1 - z$.

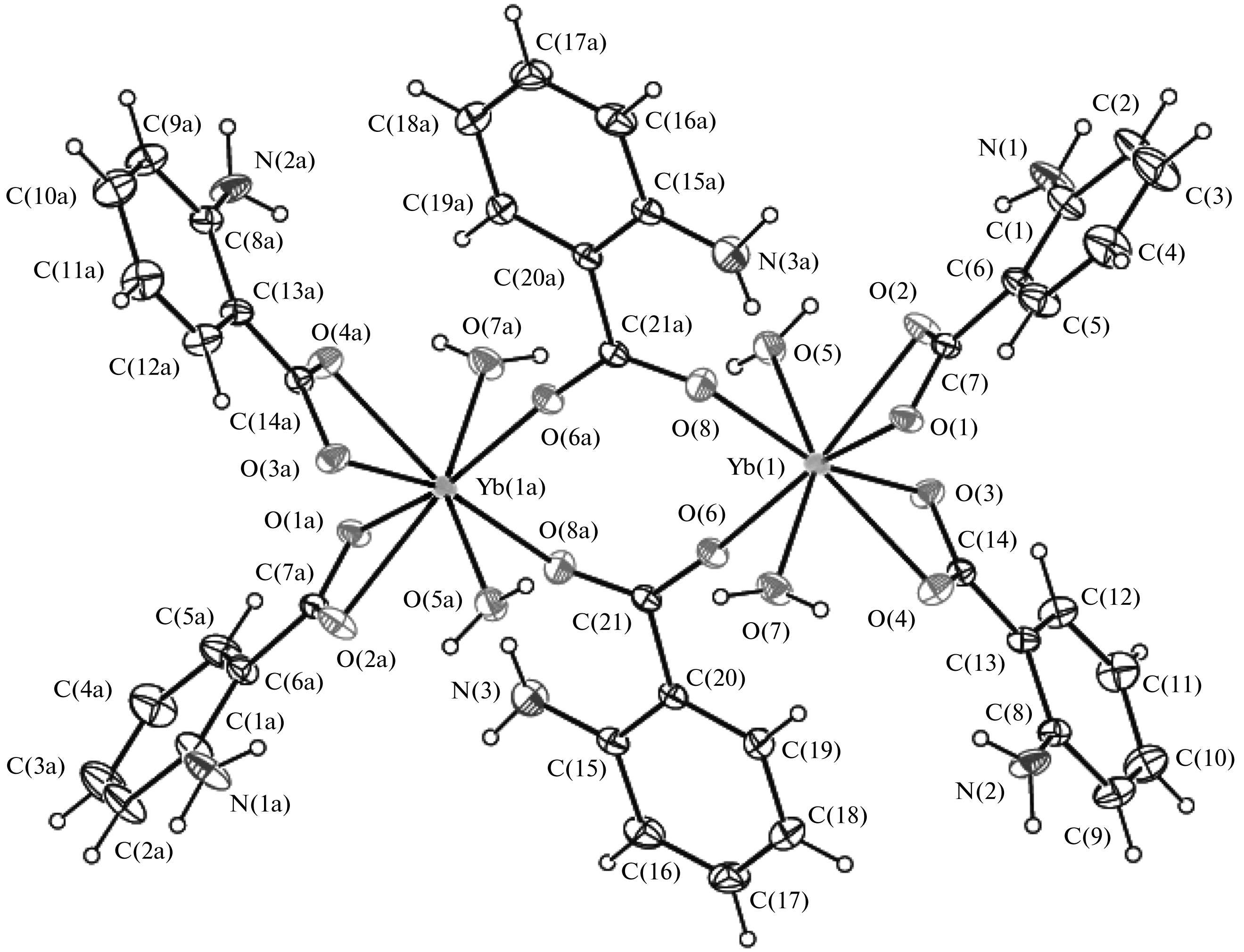

Fig. 1. The title molecule **I** showing the atom labeling scheme. Displacement ellipsoids for non-H atoms are drawn at the 30% probability level. The disordered ethanol solvent molecule was not shown for clarity.

O(1) 2.419(4), Yb(1)–O(2) 2.331(5), Yb(1)–O(3) 2.431(4), Yb(1)–O(4) 2.335(3)) and the shortest Yb---O bond involves the bidentate bridging carboxylate (Yb(1)–O(6) 2.193(4), Yb(1)–O(8) 2.236(4)). This is due to the fact, small bite angle (O(1)Yb(1)O(2) 54.58(14)°, O(3)Yb(1)O(4) 54.02(12)°) in bidentate chelate weakens the Yb---O bonding interactions [36]. The Yb---Yb bond distance is 5.095 Å which is comparable with the anticipated range of other lanthanide complexes [37, 38].

In the crystal structure of **I**, there are some intermolecular N–H···O hydrogen bonds and O–H···O hydrogen bonds as shown in Fig. 2, one weak π–π interaction between the C(1)–C(6) benzene rings (Cg1–Cg1 $(2 - x, -y, -z)$ 3.849(4) Å) and one C–H···π stacking interaction (Table 3).

The molecular structure of complex **II** is shown in Fig. 3. The binulclear complex **II** is non-centrosymmetric and is comprised of six 3AMB ligands, four coordinated water molecules and three uncoordinated water molecules. The 3AMB ligand is coordinated to the Yb^{3+} ions in two different modes: chelating and bridging with a Yb–Yb separation of 4.9250(3) Å which is comparable with the already reported lanthanide complexes [36–38]. The two Yb^{3+} ions are linked by two carboxylic groups of two ligands through their bidentate bridging modes. In **II** each Yb^{3+} ion is coordinated to eight atoms, two of which are oxygen atoms from the bridging carboxylates, four oxygen atoms from the bidentate chelating carboxylate groups and two oxygen atoms from two coordinated water molecues. The Yb^{3+} ion adopts a distorted dodecahedral geometry. The Yb–O distances are within the range of 2.219(4)–2.414(4) Å, all of which are within the range of those of other eight-coordinated Yb(III) complexes [35, 39, 40]. The longest Yb---O bond distances are from the bidentate chelating carboxylate oxygen range from 2.355 to 2.414 and the shortest Yb---O bond involves the bidentate bridging carboxylate range from 2.207 to 2.267. This is due to the fact

Table 3. Geometric parameters of hydrogen bonds for **I*** and **II****

D–H···A	Distance, Å			Angle, D–H···A, deg
	D–H	H···A	D···A	
		I		
N(3)–N(31N)···O(8)	0.85(5)	2.08(5)	2.707(6)	31(5)
O(9B)–H(9*B*)···N(1)$^{\text{i}}$	0.82	2.31	3.113(12)	167
N(1)–H(12N)···O(2)	0.85(6)	2.05(7)	2.658(9)	127(6)
N(1)–H(12N)···O(3)$^{\text{ii}}$	0.85(6)	2.56(6)	3.306(8)	146(6)
N(2)–H(21N)···O(1)$^{\text{iii}}$	0.84(6)	2.16(5)	2.926(6)	152(5)
N(2)–H(22N)···O(4)	0.85(5)	2.11(7)	2.677(6)	124(5)
O(5)–H(51*w*)···O(3)$^{\text{ii}}$	0.83(6)	1.95(6)	2.779(6)	177(8)
O(5)–H(52*w*)···O(9*B*)$^{\text{iv}}$	0.82(4)	1.95(4)	2.687(10)	150(4)
O(7)–H(71*w*)···N(2)$^{\text{iii}}$	0.83(5)	2.13(6)	2.929(7)	160(6)
O(7)–H(72*w*)···O(9*B*)	0.84(4)	1.82(5)	2.647(12)	172(7)
C(11)–H(11)···Cg(3)$^{\text{ii}}$	0.93	2.86	3.692(8)	149
		II		
N(2A)–H(2*A*1)···N(4)$^{\text{i}}$	0.91(6)	2.47(6)	3.360(13)	166(5)
N(1)–H(1*B*)···O(6)$^{\text{ii}}$	0.90(5)	2.23(5)	3.005(7)	145(3)
N(3)–H(3*A*)···O(18)$^{\text{iii}}$	0.96(2)	2.32(4)	3.213(10)	155(5)
N(4)–H(4*B*)···O(14)$^{\text{iv}}$	0.89(6)	2.59(8)	3.162(7)	123(6)
N(5)–H(5*A*)···O(19)$^{\text{v}}$	0.89(6)	2.23(6)	3.122(12)	177(9)
N(6B)–H(6*B*1)···N(3)$^{\text{vi}}$	0.92(6)	2.31(9)	2.948(11)	126(9)
O(7)–H(7*A*)···O(12)	0.93	2.2200	2.671(5)	109.00
O(7)–H(7*A*)···N(1)$^{\text{iv}}$	0.93	2.1500	2.974(8)	146.00
N(6B)–H(6*B*2)···O(11)$^{\text{vii}}$	0.91(4)	2.46(4)	3.366(8)	178(14)
O(8)–H(8*A*)···O(19)	0.93	2.0300	2.862(10)	148.00
O(8)–H(8*B*)···O(9)$^{\text{vi}}$	0.93	1.8900	2.711(5)	145.00
O(15)–H(15*A*)···O(18)	0.86(7)	1.96(7)	2.796(12)	166(6)
O(15)–H(15*B*)···O(3)$^{\text{viii}}$	0.84(5)	1.93(5)	2.756(6)	166(7)
O(16)–H(16*A*)···O(2)$^{\text{viii}}$	0.85(6)	1.91(6)	2.756(5)	177(6)
O(16)–H(16*B*)···N(5)$^{\text{ix}}$	0.85(6)	1.97(6)	2.817(8)	173(4)
O(17)–H(17*A*)···O(19)$^{\text{viii}}$	0.85(9)	2.43(14)	3.003(13)	126(12)
O(18)–H(18*A*)···O(17)	0.86(5)	2.41(4)	2.895(14)	116(3)
C(28)–H(28)···O(10)	0.93	2.5100	2.812(6)	100.00
C(28)–H(28)···O(1)$^{\text{iv}}$	0.93	2.5100	3.379(7)	156.00
C(38*B*)–H(38*B*)···O(130)	0.93	2.3100	2.669(9)	102.00

* Symmetry codes: $^{\text{i}}\,-1 + x, y, z$; $^{\text{ii}}\,2 - x, -y, 1 - z$; $^{\text{iii}}\,2 - x, 1 - y, 1 - z$; $^{\text{iv}}\,1 - x, -y, 1 - z$.

** Symmetry codes: $^{\text{i}}\,1 - x, 1 - y, -z$; $^{\text{ii}}\,3/2 - x, 1/2 + y, 1/2 - z$; $^{\text{iii}}\,-1/2 + x, 1/2 - y, -1/2 + z$; $^{\text{iv}}\,3/2 - x, -1/2 + y, 1/2 - z$; $^{\text{v}}\,1 + x, y, z$; $^{\text{vi}}\,1/2 - x, 1/2 + y, 1/2 - z$; $^{\text{vii}}\,1 - x, 1 - y, 1 - z$; $^{\text{viii}}\,1/2 - x, -1/2 + y, 1/2 - z$; $^{\text{ix}}\,-1 + x, y, z$.

the small bite angle (O(1)Yb(2)O(2) 55.16(12)°, O(3)Yb(2)O(4) 54.33(15)°, O(9)Yb(1)O(10) 54.35(12)°, O(11)Yb(1)O(12) 54.25(12)°) in bidentate chelate weakens the Yb---O bonding interactions [36]. Futhermore, Yb–O bond length for the coordinated water molecules are (Yb(2)–O(7) 2.330(4), Yb(2)–O(8) 2.320(4), Yb(1)–O(15) 2.302(5), Yb(1)–O(16) 2.285(5) Å) comparatively smaller than the chelating carboxylate but larger than the bridging carboxylate [38, 41].

The crystal structures of II is also stabilized by N–H···O, O–H···O, O–H···N, and C–H···O hydrogen

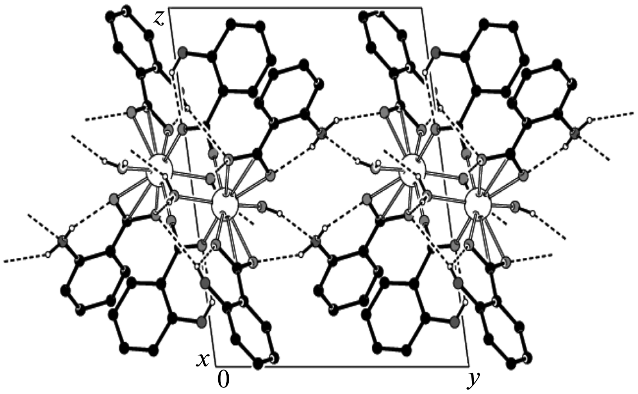

Fig. 2. View of the packing and hydrogen bonding of **I** down a-axis. The disordered ethanol solvent molecule was not shown for clarity.

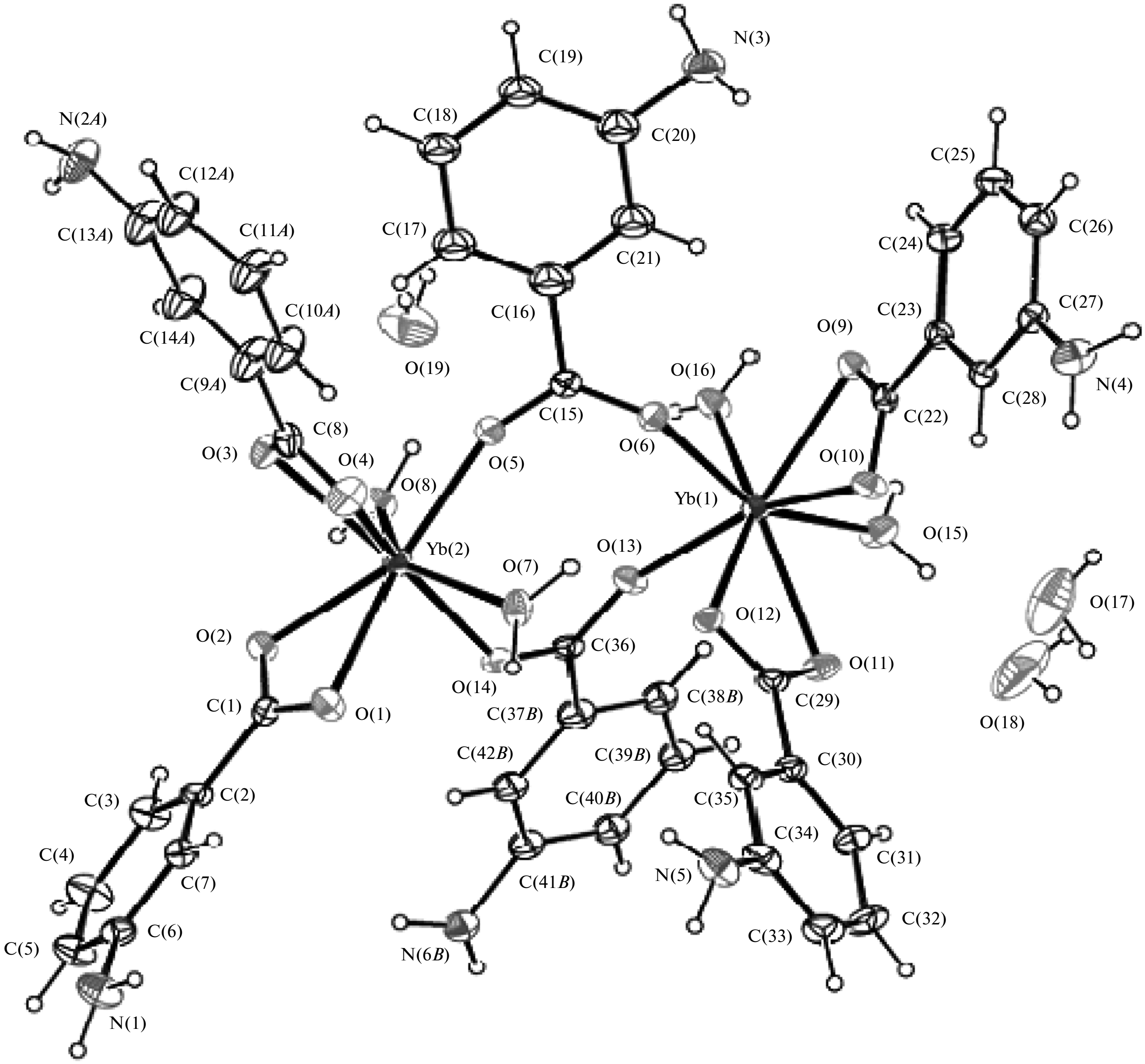

Fig. 3. Complex **II** with the atom numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 20% probability level. Only the major disorder component is shown.

bonds, C—H···π interactions (Table 3) and π—π-stacking interactions (centroid-centroid distances 3.598(6) and 3.612(8) Å). The crystal structure of complex **II** contain the voids of 62.3 $Å^3$ per unit cell, respectively.

ACKNOWLEDGEMENTS

S. Hussain greatfully acknowledges the Higher Education Commission of Pakistan (HEC) for providing the financial support through Indigenous 5000 PhD Fellowship Program.

REFERENCES

1. Molander, G.A. and Romero, J.A.C., *Chem. Rev.*, 2002, vol. 102, no. 6, p. 2161.
2. Lu, E., Yuan, Y., Chen, Y., and Xia, W., *ACS Catalysis*, 2013, vol. 3, no. 4, p. 521.
3. Gai, Y.-L., Jiang , F.-L., Chen, L., et al., *Inorg. Chem.*, 2013, vol. 52, no. 13, p. 7658.
4. Yan, B. and Zhu, H., *J. Fluoresc.*, 2007, vol. 17, no. 3, p. 331.
5. Terai, T., Kikuchi, K., Iwasawa, S.-Y., et al., *J. Am. Chem. Soc.*, 2006, vol. 128, no. 21, p. 6938.
6. Dos Santos, C.M.G., Harte, A.J., Quinn, S.J., and Gunnlaugsson, T., *Coord. Chem. Rev.*, 2008, vol. 252, nos. 23–24, p. 2512.
7. Wang, Y.-W., Zhang, Y.-L., Dou, W., et al., *Dalton Trans.*, 2010, vol. 39, no. 38, p. 9013.
8. Bettencourt-Dias, Ad. and Viswanathan, S., *Dalton Trans.*, 2006, vol. 34, p. 4093.
9. Heffeter, P., Jakupec, M.A., Korner, W., et al., *Biochem. Pharmacol.*, 2006, vol. 71, no. 4, p. 426.
10. Sessler, J.L., Dow, W.C., O'Connor, D., et al., *J. Alloy. Compd.*, 1997, vol. 249, nos. 1–2, p. 146.
11. Yam, V.W.-W. and Lo, K.K.-W., *Coord. Chem. Rev.*, 1999, vol. 184, no. 1, p. 157.
12. Oyang, L., Sun, H.-L., Wang, X.-Y., et al., *J. Mol. Struct.*, 2005, vol. 740, nos. 1–3, p. 175.
13. Tian, J., Li, B., Zhang, X., et al., *Dalton Trans.*, 2013, vol. 42, no. 23, p. 8504.
14. Hou, G.-F., Li, H.-X., and Li, W.-Z., et al., *Cryst. Growth Des.*, 2013, vol. 13, no. 8, p. 337.
15. Charbonnière, L.J., Weibel, N., Retailleau, P., and Ziessel, R., *Chem. Eur. J.,* 2007, vol. 13, no. 1, p. 346.
16. Tsaryuk, V., Zhuravlev, K., Zolin, V., et al., *J. Photochem. Photobiol., A*, 2006, vol. 177, nos. 2–3, p. 314.
17. Hilder, M., Junk, P.C., Kynast, U.H., and Lezhnina, M.M., *J. Photochem. Photobiol., A*, 2009, vol. 202, no. 1, p. 10.
18. Dong, H.-L. and Xu, L., *Inorg. Chem. Commun.*, 2006, vol. 9, no. 4, p. 379.
19. Feng, R., Jiang, F.-L., Wu, M.-Y., et al., *Cryst. Growth Des.*, 2010, vol. 10, no. 5, p. 2306.
20. Xie, Y., Xing, Y.-H., Wang, Z., et al., *Inorg. Chim. Acta*, 2010, vol. 363, no 5, p. 918.
21. Ye, J., Wan, Q., Gao, H., et al., *Inorg. Chim. Acta*, 2012, vol. 384, p. 1.
22. Zhao, L., Chen, Y., Zhang, H., et al., *J. Mol. Struct.,* 2009, vol. 920, nos. 1–3, p. 441.
23. Pan, L., Huang, X., Li, J., et al., *Angew. Chem. Int. Ed.*, 2000, vol. 39, no. 3, p. 527.
24. Sheldrick, G., *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, vol. 64, no. 1, p. 112.
25. Farrugia, L., *J. Appl. Cryst.*, 1997, vol. 30, no. 5, p. 565.
26. Song, Y., Yan, B., and Chen, Z., *J. Coord. Chem.*, 2005, vol. 58, no. 8, p. 647.
27. Chen, W. and Fukuzumi, S., *Inorg. Chem.*, 2009, vol. 48, no. 8, p. 3800.
28. Cheng, J.-W., Zheng, S.-T., Ma, E., and Yang, G.-Y., *Inorg. Chem.*, 2007, vol. 46, no. 25, p. 10534.
29. Gu, G.-L., Tang, R.-R., Zheng, Y.-H., and Shi, X.-M., *Spectrochim. Acta, A*, 2008, vol. 71, no. 1, p. 209.
30. Hu, M., Yao, J., and Su, H., *J. Cluster Sci.*, 2010, vol. 21, no. 4, p. 691.
31. Qingyue, S., Chunhua, L., Yaru, N., et al., *J. Rare Earths*, 2007, vol. 25, no. 5, p. 549.
32. Singh, G.S. and Pheko, T., *Spectrochim. Acta, A*, 2008, vol. 70, no. 3, p. 595.
33. Nawrocka, J. and Patroniak, V., *J. Alloy. Compd.*, 2004, vol. 380, nos. 1–2, p. 159.
34. Cheng, J.-W., Zheng, S.-T., and Yang, G.-Y., *Inorg. Chem.*, 2008, vol. 47, no. 11, p. 4930.
35. Shen, J.-B., Liu, J.-L., and Zhao, G.-L., *Acta Crystallogr., Sect. E: Structure Reports Online*, 2011, vol. 67, no. 10, p. 1361.
36. Jia, G., Law, G.-L., Wong, K.-L., et al., *Inorg. Chem.*, 2008, vol. 47, no. 20, p. 9431.
37. Mao, J.-G., Zhang, H.-J., Ni, J.-Z., et al., *Polyhedron*, 1998, vol. 17, nos. 23–24, p. 3999.
38. Ramya, A.R., Reddy, M.L.P., Cowley, A.H., and Vasudevan, K.V., *Inorg. Chem.*, 2010, vol. 49, no. 5, p. 2407.
39. Liang Ping, W., Munakata, M., Kuroda-Sowa, T., et al., *Inorg. Chim. Acta*, 1996, vol. 249, no. 2, p. 183.
40. Cao, R., Sun, D., Liang, Y., et al., *Inorg. Chem.*, 2002, vol. 41, no. 8, p. 2087.
41. Sun, H.-L., Ye, C.-H., Wang, X.-Y., et al., *J. Mol. Struct.*, 2004, vol. 702, nos. 1–3, p. 77.