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Synthesis and Structures of Nine-Coordinate $K[Dy(Edta)(H_2O)_3] \cdot 3.5H_2O$, $(NH_4)_3[Dy(Ttha)] \cdot 5H_2O$, and Eight-Coordinate $NH_4[Dy(Cydta)(H_2O)_2] \cdot 4.5H_2O$ Complexes[1]

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Abstract—The title complexes, $K[Dy(Edta)(H_2O)_3] \cdot 3.5H_2O$ (I) (H_4Edta = ethylenediamine-N,N,N',N'-tetraacetic acid), $(NH_4)_3[Dy(Ttha)] \cdot 5H_2O$ (II) (H_6Ttha = triethylenetetramine-N, N,N',N'',N''',N'''-hexaacetic acid), and $NH_4[Dy(Cydta)(H_2O)_2] \cdot 4.5H_2O$ (III) (H_4Cydta = *trans*-1,2-cyclohexanediamine-N,N,N',N'-tetraacetic acid), were prepared, and their compositions and structures were determined by elemental analyses and single-crystal X-ray diffraction techniques, respectively. In complex I, the Dy^{3+} ion is nine-coordinated by an Edta ligand and three water molecules, yielding a pseudo-monocapped square antiprismatic conformation, and the complex crystallizes in the orthorhombic crystal system with space group $Fdd2$. The crystal data are as follows: $a = 19.751(7)$, $b = 35.573(12)$, $c = 12.227(4)$ Å, $V = 8591(5)$ Å^3, $Z = 16$, space group $Fdd2$ $\rho_c = 1.877$ g/cm^3, $\mu = 3.742$ mm^{-1}, $F(000) = 4800$, $R = 0.0259$, and $wR = 0.0616$ for 3218 observed reflections with $I \ge 2\sigma(I)$. For complex II, the Dy^{3+} ion is nine-coordinated by a Ttha ligand, yielding a pseudo-monocapped square antiprismatic conformation, and the complex crystallizes in the monoclinic crystal system with space group $P2_1/c$. In addition, there is a free non-coordinate carboxyl group ($–CH_2COO^–$) in the $[Dy(Ttha)]^{3–}$ complex anion. The crystal data are as follows: $a = 10.353(3)$, $b = 12.746(4)$, $c = 23.141(7)$ Å, $\beta = 91.005(5)°$, $V = 3053.2(15)$ Å^3, $Z = 4$, space group $P2_1/c$ $\rho_c = 1.730$ g/cm^3, $\mu = 2.532$ mm^{-1}, $F(000) = 1620$, $R = 0.0332$ and $wR = 0.0924$ for 5390 observed reflections with $I \ge 2\sigma(I)$. For complex III, the Dy^{3+} ion is eight-coordinated by a ligand Cydta and two water molecules, yielding a distorted square antiprismatic conformation, and the complex crystallizes in the triclinic system with space group $P\bar{1}$. The crystal data are as follows: $a = 8.604(3)$, $b = 10.012(4)$, $c = 14.369(6)$ Å, $\alpha = 88.330(6)°$, $\beta = 75.363(6)°$, $\gamma = 88.285(6)°$, space group $P\bar{1}$ $V = 1196.9(8)$ Å^3, $Z = 2$, $\rho_c = 1.776$ g/cm^3, $\mu = 3.194$ mm^{-1}, $F(000) = 644$, $R = 0.0445$ and $wR = 0.1041$ for 3931 observed reflections with $I \ge 2\sigma(I)$.

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Much progress has been achieved in the coordination chemistry of rare-earth (**RE**) metals for two decades. This resurgence of interest may be related to the applications of rare-earth metals for different purposes, and in the research and development of new materials. Now, many RE^{3+} ions are widely used in the medicine field for their anti-inflammatory and antineoplastic activities [1–5]. The Dy^{3+} ion is one of them, whose complexes have strong antibacterial activities [6]. At the same time, because of the desirable physical characteristics and ready availability, the Dy^{3+} (also including Sm^{3+}, Ho^{3+}, and Lu^{3+}) complexes have been used for the palliative treatment of pain from metastatic bone cancer, radiation synovectomy, and radioimmunotherapy [7–9]. Moreover, the complexes of the Dy^{3+} ion with much shorter electronic relaxation times are effective NMR shift reagents [10–14]. Therefore, it is meaningful to research the biological effects and coordination states of the Dy^{3+} ion and other RE^{3+} ions.

It is well known that the aminopolycarboxylic acid ligands can form stable and water-soluble complexes with all RE^{3+} ions. In general, the coordination structure and coordination number of RE^{3+} metal complexes depend on the ionic radii, electron configurations, valent states of central metals, and shapes of the aminopolycarboxylic acid ligands. In addition, RE^{3+} ions often form eight-, nine-, and ten-coordinate complexes with aminopolycarboxylic acid ligands. Taking RE^{3+} complexes of Edta (H_4Edta = ethylenedianine-N,N,N',N'-tetraacetic acid) and Ttha (H_6Ttha = triethylenetetramine-N,N,N',N'',N''',N'''-hexaacetic acid) ligands, for example, La^{3+} and Ce^{3+} ions with particularly large ionic radii and few *f*-orbital electrons can form ten-coordinate complexes. Contrarily, Tm^{3+},

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Yb^{3+}, and Lu^{3+} ions with much smaller radii and more *f*-orbital electrons only select eight-coordinate complexes. The rest of Eu^{3+}, Gd^{3+}, Tb^{3+}, Dy^{3+}, Ho^{3+}, and Er^{3+} ions can form nine-coordinate complexes [15–22]. Generally, for the RE^{3+} complexes with Ttha ligand, due to slightly high acidity (pH 4.5–5.5), there is a noncoordinate carboxyl group ($–CH_2COOH$). Such complexes usually reveal weak acidity in aqueous solutions. If it adjusts pH of the solution properly to the approximate neutral conditions, maybe the neutral RE^{3+} complexes will be more suitable for application in vivo. Otherwise, being different from the Edta and Ttha ligands, there is a rigid six-membered ring in Cydta (H_4Cydta = *trans*-1.2-cyclohexanediaminete-N,N,N',N'-tetraacetic acid) ligand. We consider that such a rigid ring may affect the coordinate structure of RE^{3+} complexes. Therefore, in order to verify the inference and research the application in the medicine field, a series of Dy^{3+} complexes with aminopolycarboxylic acid ligands were synthesized to compare their molecular and crystal structures.

EXPERIMENTAL

Synthesis of K[Dy(Edta)(H_2O)$_3$] · 3.5H_2O (I). Colorless crystals of complex **I** were prepared by mixing H_4Edta (1.4612 g, 5.0 mmol) and Dy_2O_3 (0.9325 g, 2.5 mmol) powders in 100 ml of water. The mixed solution was heated under stirring and refluxing. After 6.0 h, the solution became transparent, and then the pH was adjusted to 6.0 by a $KHCO_3$ aqueous solution. Finally, the solution was concentrated to 25 ml and left to evaporate slowly at room temperature.

For $C_{10}H_{25}N_2O_{14.5}DyK$
anal. calcd, %: Dy, 26.77; C, 19.79; H, 4.15; N, 4.62; K, 6.44.
Found, %: Dy, 26.75; C, 19.82; H, 4.17; N, 4.63; K, 6.42.

Synthesis of (NH_4)$_3$[Dy(Ttha)] · 5H_2O (II). Colorless crystals of complex **II** were prepared by mixing H_6Ttha (2.4715 g, 5.0 mmol) and Dy_2O_3 (0.9325 g, 2.5 mmol) powders in 100 ml of water. The mixed solution was heated under stirring and refluxing. After 15.0 h, the solution became transparent, and then the pH was adjusted to 6.8 by aqueous NH_3. Finally, the solution was concentrated to 25 ml and left to evaporate slowly at room temperature.

For $C_{18}H_{46}N_7O_{17}Dy$
anal. calcd, %: Dy, 20.44; C, 27.19; H, 5.83; N, 12.33.
Found, %: Dy, 20.41; C, 27.21; H, 5.82; N, 12.32.

Synthesis of NH_4[Dy(Cydta)(H_2O)$_2$] · 4.5H_2O (III). Colorless crystals of complex **III** were prepared by mixing H_4Cydta (1.8218 g, 5.0 mmol) and Dy_2O_3 (0.9325 g, 2.5 mmol) powders in 100 ml of water. The mixed solution was heated under stirring and refluxing. After 7.0 h, the solution became transparent, and then the pH was adjusted to 6.0 by aqueous NH_3. Finally, the solution was concentrated to 25 ml and left to evaporate slowly at room temperature.

For $C_{14}H_{35}N_3O_{14.5}Dy$
anal. calcd, %: Dy, 25.39; C, 26.27; H, 5.51; N, 6.57.
Found, %: Dy, 25.40; C, 26.29; H, 5.48; N, 6.60.

The brutto-formula of complexes **I–III** are approximately consistent with the results of diffraction analysis.

X-ray structure determination. X-ray intensity data were collected at room temperature (293(2) K) on a Bruker SMART CCD type X-ray diffractometer with graphite-monochromatized MoK_α radiation (λ = 0.71073 Å). The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares methods on F^2. All calculations were performed by the SHELXTL-97 program package on PDP11/44 and Pentium MMX/166 computers. The crystal data and structure refinement for the three complexes are listed in Table 1. The selected bond distances and bond angles of three complexes are listed in Table 2. The molecular structures of complexes **I**, **II**, and **III** are illustrated in Figs. 1 and their molecular packings in a unit cell are shown in Figs. 2.

Supplementary material has been deposited with the Cambridge Crystallographic Data Centre (nos. 693480 (**I**), 176973 (**II**), 693479 (**III**); deposit@ccdc.cam.ac.uk or www:http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

As shown in Fig. 1a, in complex **I**, the central Dy^{3+} ion is nine-coordinate by an Edta ligand and three water molecules. The nine donor atoms, including four carboxyl oxygen atoms and two amine nitrogen atoms, which come from the same Edta ligand, and three oxygen atoms from three coordinate water molecules, yield a pseudo-monocapped square antiprismatic conformation. The average Dy–O bond distance is 2.406(5) Å, with the longest one being 2.504(4) Å (Dy–O(1*w*)) and the shortest one being 2.344(5) Å (Dy–O(5)). The Dy–N bond distances are longer than Dy–O. The average bond distance of Dy–N is 2.658(6) Å, with the longest one being 2.665(6) Å (Dy–N(1)) and the shortest one being 2.650(5) Å (Dy–N(2)).

According to Muetterties and Guggenbergers' definition for nine-coordinate complexes [23, 24], two idealized polyhedra should be C_{4v} monocapped square antiprism and D_{3h} tricapped trigonal prism. The torsion angle of the bottom plane is important to judge which conformation the polyhedron adopts. It is the dihedral angle between two trigonal planes, which is 0°C for C_{4v} monocapped square antiprism, but 26.4° for D_{3h} tricapped trigonal prism. The torsion angle is 11.13° between O(7)O(2*w*)O(5) and O(1*w*)O(2*w*)O(5), and 12.24° between O(5)O(1*w*)O(7) and O(2*w*)O(1*w*)O(7).

Table 1. Crystal data and structure refinement for **I**, **II**, and **III**

Parameter	Value		
	I	**II**	**III**
M	606.92	795.12	639.95
Crystal system	Orthorhombic	Monoclinic	Triclinic
Space group	$Fdd2$	$P2_1/c$	$P\bar{1}$
Unit cell dimensions:			
a, Å	19.751(7)	10.353(3)	8.604(3)
b, Å	35.573(12)	12.746(4)	10.012(4)
c, Å	12.227(4)	23.141(7)	14.369(6)
α, deg	90	90	88.330(6)
β, deg	90	91.005(5)	75.363(6)
γ, deg	90	90	88.285(6)
Volume, Å^3	8591(5)	3053.2(15)	1196.9(8)
Z	16	4	2
ρ_{calcd}, mg/cm^3	1.877	1.730	1.776
Absorption coefficient, mm^{-1}	3.742	2.532	3.194
F(000)	4800	1620	644
Crystal size, mm	0.22 × 0.20 × 0.20	0.25 × 0.20 × 0.20	0.25 × 0.15 × 0.10
θ range for data collection, deg	1.14 to 26.41	1.76 to 25.03	1.47 to 25.05
Limiting indices	$-24 \le h \le 19$	$-12 \le h \le 11$	$-10 \le h \le 9$
	$-43 \le k \le 44$	$-15 \le k \le 14$	$-11 \le k \le 6$
	$-15 \le l \le 8$	$-25 \le l \le 27$	$-15 \le l \le 17$
Reflections collected	10107	12395	5064
Independent reflections	3218 (R_{int} = 0.0343)	5390 (R_{int} = 0.0312)	3931 (R_{int} = 0.0331)
Completeness to θ_{max}, %	99.5	99.9	92.8
Goodness-of-fit on F^2	1.025	1.065	1.079
Final R indices ($I > 2\sigma(I)$)	R_1 = 0.0259, wR_2 = 0.0616	R_1 = 0.0332, wR_2 = 0.0924	R_1 = 0.0445, wR_2 = 0.1041
R indices (all data)	R_1 = 0.0312, wR_2 = 0.0637	R_1 = 0.0460, wR_2 = 0.1012	R_1 = 0.0608, wR_2 = 0.1202
Largest difference peak and hole, e Å^{-3}	1.019 and –0.797	0.692 and –0.801	1.178 and –1.358

Therefore, it is considered that the coordinating polyhedron of complex **I** adopts a pseudo-C_{4v} monocapped square antiprismatic conformation, a common conformation for nine-coordinate RE^{3+} metal complexes with aminopolycarboxylic acid ligands. The top tetragon plane is composed of N(2), O(2), O(6*w*), and O(4), and the bottom tetragon plane is composed of O(5), O(7), O(1*w*), and O(2*w*), which form a square antiprism. The capped position above the top tetragon plane is occupied by N(1). Because of the mutual repulsion between the top plane and the capped nitrogen atom, the bond length of Dy–N(1) is the longest of all the coordination bonds. As a hexadentate ligand, each Edta coordinates to a single Dy^{3+} ion with its six donor atoms. As a result, five five-membered rings form. The atoms of each five-membered ring are almost coplanar.

As shown in Fig. 2a, complex **I** crystallizes in the orthorhombic system, space group $Fdd2$ with sixteen complex molecules in a unit cell. The $[Dy(Edta)(H_2O)_3]^-$ complex anions are connected by potassium cations and hydrogen bonds, which play very important role in stabilizing the crystal structure. As the bridge, each K$^+$ cation connects two $[Dy(Edta)(H_2O)_3]^-$ complex anions. K$^+$ is nine-coordinated by nine oxygen atoms, including one non-coordinate and two coordinate O atoms from the carboxyl groups of two adjacent Edta ligands, two O atoms from coordinate water molecules, and the rest O atoms from four crystallization water molecules. The crystallization water molecules, coordinate water molecules, and coordinate and non-coordinate O atoms of the Edta ligands are linked through hydrogen bonds in a unit

Table 2. Selected bond distances (Å) and angles (deg) of **I**, **II**, and **III***

Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å
I					
Dy–O(2)	2.350(5)	Dy–O(7)	2.371(5)	Dy–O(6*w*)	2.408(5)
Dy–O(4)	2.406(4)	Dy–O(1*w*)	2.504(4)	Dy–N(1)	2.665(6)
Dy–O(5)	2.344(5)	Dy–O(2*w*)$^{\#1}$	2.456(4)	Dy–N(2)	2.650(5)
II					
Dy–O(3)	2.346(4)	Dy–O(9)	2.336(4)	Dy–N(2)	2.712(4)
Dy–O(5)	2.300(4)	Dy–O(11)	2.406(3)	Dy–N(3)	2.680(4)
Dy–O(8)	2.309(4)	Dy–N(1)	2.672(4)	Dy–N(4)	2.609(4)
III					
Dy–O(1)	2.311(6)	Dy–O(7)	2.327(6)	Dy–N(1)	2.564(7)
Dy–O(3)	2.323(6)	Dy–O(9)	2.369(6)	Dy–N(2)	2.561(6)
Dy–O(5)	2.316(6)	Dy–O(10)	2.349(6)		
Angle	ω, deg	Angle	ω, deg	Angle	ω, deg
I					
O(2)DyO(4)	129.61(15)	O(5)DyO(2)	76.95(18)	O(7)DyN(1)	113.73(18)
O(2)DyO(7)	138.52(16)	O(5)DyO(4)	141.22(17)	O(7)DyN(2)	66.15(18)
O(2)DyO(1*w*)	73.12(16)	O(5)DyO(7)	71.32(18)	O(1w)DyN(1)	128.27(17)
O(2)DyO(2*w*)$^{\#1}$	142.02(16)	O(5)DyO(1*w*)	69.82(16)	O(1w)DyN(2)	131.75(15)
O(2)DyO(6*w*)	79.27(17)	O(5)DyO(2*w*)$^{\#1}$	104.92(18)	O(2w)$^{\#1}$DyO(1*w*)	72.27(15)
O(2)DyN(1)	66.18(16)	O(5)DyO(6*w*)	138.50(17)	O(2w)$^{\#1}$DyN(1)	128.23(16)
O(2)DyN(2)	77.28(18)	O(5)DyN(1)	126.35(17)	O(2w)$^{\#1}$DyN(2)	139.22(18)
O(4)DyO(1*w*)	138.27(15)	O(5)DyN(2)	66.90(17)	O(6w)DyO(1*w*)	70.96(17)
O(4)DyO(2*w*)$^{\#1}$	72.19(15)	O(7)DyO(4)	70.94(16)	O(6*w*)DyO(2*w*)$^{\#1}$	75.11(15)
O(4)DyO(6*w*)	79.37(16)	O(7)DyO(1*w*)	117.86(17)	O(6*w*)DyN(1)	71.29(18)
O(4)DyN(1)	63.84(15)	O(7DyO(2*w*)$^{\#1}$	73.36(16)	O(6*w*)DyN(2)	138.41(19)
O(4)DyN(2)	89.83(15)	O(7)DyO(6*w*)	141.83(17)	N(2)DyN(1)	67.94(18)
II					
O(3)DyO(5)	125.47(13)	O(5)DyN(2)	64.84(13)	O(9)DyN(3)	72.61(14)
O(3)DyO(8)	76.34(12)	O(5)DyN(3)	99.18(14)	O(9)DyN(4)	67.00(13)
O(3)DyO(9)	74.00(13)	O(5)DyN(4)	75.98(13)	O(11)DyN(1)	94.75(13)
O(3)DyO(11)	73.37(12)	O(8)DyO(9)	74.76(13)	O(11)DyN(2)	136.59(13)
O(3)DyN(1)	64.12(12)	O(8)DyO(11)	147.51(13)	O(11)DyN(3)	132.03(12)
O(3)DyN(2)	124.66(13)	O(8)DyN(1)	82.30(13)	O(11)DyN(4)	63.67(13)
O(3)DyN(3)	135.07(13)	O(8)DyN(2)	71.96(13)	N(1)DyN(2)	67.59(13)
O(3)DyN(4)	122.68(13)	O(8)DyN(3)	66.50(13)	N(1)DyN(3)	130.53(13)
O(5)DyO(8)	136.55(13)	O(8)DyN(4)	127.42(13)	N(1)DyN(4)	149.78(13)
O(5)DyO(9)	142.59(13)	O(9)DyO(11)	85.76(13)	N(2)DyN(3)	66.71(13)
O(5)DyO(11)	72.87(13)	O(9)DyN(1)	135.88(13)	N(2)DyN(4)	112.62(14)
O(5)DyN(1)	77.50(13)	O(9)DyN(2)	134.93(13)	N(3)DyN(4)	68.48(13)
III					
O(1DyO(3)	104.2(2)	O(3)DyN(1)	69.5(2)	O(7)DyN(1)	132.6(2)
O(1)DyO(5)	85.2(2)	O(3)DyN(2)	75.1(2)	O(7)DyN(2)	67.4(2)
O(1)DyO(7)	158.5(2)	O(5)DyO(3)	136.7(2)	O(9)DyN(1)	142.6(2)
O(1)DyO(9)	87.1(2)	O(5)DyO(7)	106.2(2)	O(9)DyN(2)	119.4(2)
O(1)DyO(10)	77.0(2)	O(5)DyO(9)	75.0(2)	O(10)DyO(9)	75.3(2)
O(1)DyN(1)	67.3(2)	O(5)DyO(10)	145.9(2)	O(10)DyN(1)	121.2(2)
O(1)DyN(2)	134.0(2)	O(5)DyN(1)	76.1(2)	O(10)DyN(2)	142.4(2)
O(3)DyO(7)	80.3(2)	O(5)DyN(2)	68.8(2)	N(2)DyN(1)	69.9(2)
O(3)DyO(9)	146.3(2)	O(7)DyO(9)	78.7(2)		
O(3)DyO(10)	76.5(2)	O(7)DyO(10)	83.9(2)		

* Symmetry codes: $^{\#1}$ $x + 1/4$, $-y + 1/4$, $z + 1/4$.

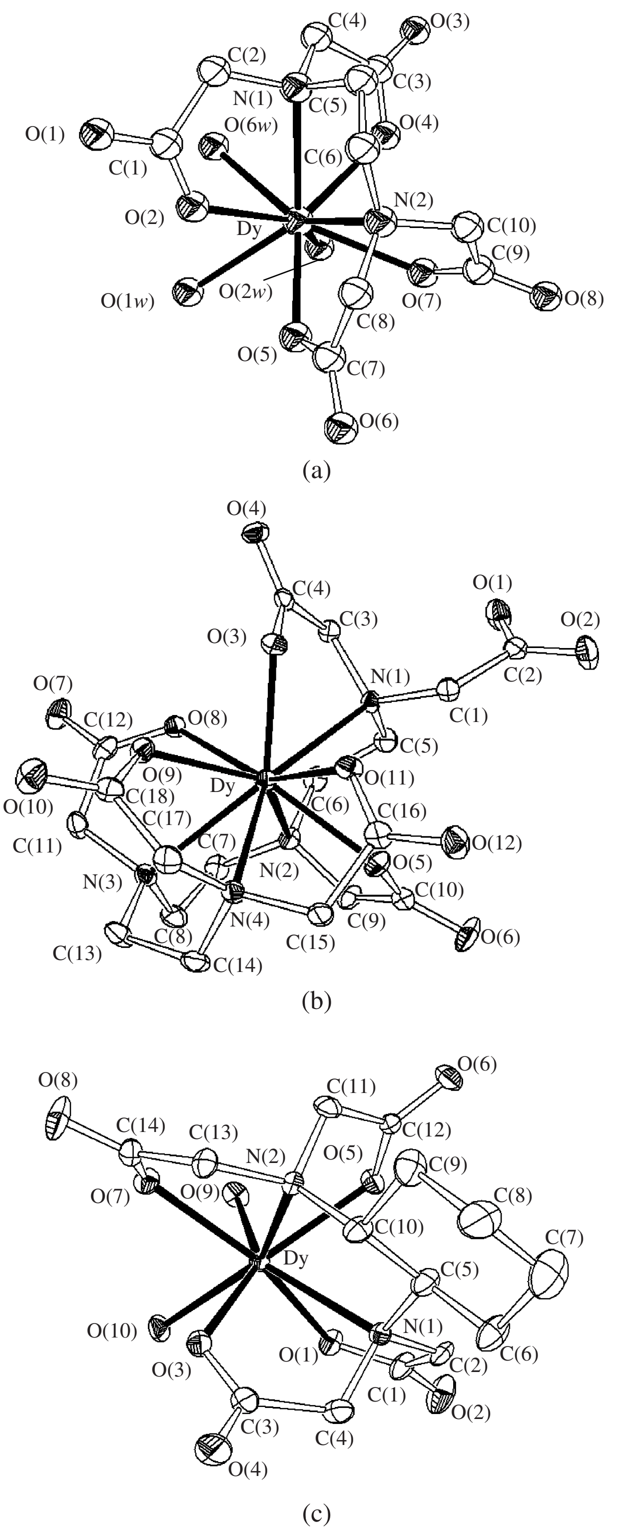

Fig. 1. Molecular structure of complex **I** (a), **II** (b), and **III** (c).

cell. Here, the hydrogen bonds, among coordinate water molecules and coordinate, as well as non-coordinate O atoms of the neighbor ligands Edta, advantage the stabilization of the crystal structure. Therefore, a layered structure is formed through hydrogen bonds and electrostatic actions.

For complex **II**, the central Dy^{3+} ion is nine-coordinated by a Ttha ligand shown in Fig. 1b. The nine donor atoms, including five carboxyl oxygen atoms and four amine nitrogen atoms, which come from the same Ttha ligand, yield a pseudo-monocapped square antiprismatic conformation. The average Dy–O bond distance is 2.339(4) Å, with the longest one being 2.406(3) Å (Dy–O(11)) and the shortest one being 2.300(4) Å (Dy–O(5)). The Dy–N bond distances are longer than Dy–O. The average bond distance of Dy–N is 2.668(4) Å, with the longest one being 2.712(4) Å (Dy–N(2)) and the shortest one being 2.609(4) Å (Dy–N(4)). In the $[Dy(Ttha)]^{3-}$ complex anion, all coordination sites around the Dy^{3+} ion are occupied by a Ttha ligand, and there is no coordinate water molecule.

In addition, the torsion angle is 6.56° between N(4)N(3)O(5) and N(2)N(3)O(5), 7.64° between N(3)N(2)N(4) and O(5)N(2)N(4). Therefore, it is considered that the coordinating polyhedron of complex **II** adopts a pseudo-C_{4v} monocapped square antiprismatic conformation just like complex **I**. The top tetragon plane is composed of N(1), O(8), O(9), and O(11), and the bottom tetragon plane is composed of N(2), N(3), N(4), and O(5), which form a square antiprism. The O(3) atom as the cap lies above the top plane. As a decadentate ligand, each Ttha coordinates to a single Dy^{3+} ion with its nine donor atoms. There is a non-coordinate free carboxyl group in the $[Dy(Ttha)]^{3-}$ complex anion. Due to the approximate neutral conditions of the solution, H^+ in $–CH_2COOH$ is lost .The non-coordinate free carboxyl group ($–CH_2COO^-$) can be modified chemically. For example, it can be used to link the complex to some biological molecules with a specific function such as that of a drug.

As shown in Fig. 2b, complex **II** crystallizes in the monoclinic system, space group $P2_1/c$ with four complex molecules in a unit cell. The $[Dy(Ttha)]^{3-}$ complex anions are connected by ammonium cations and hydrogen bonds, which play very important roles in stabilizing the crystal structure. As the bridge, N(5) and N(6) of ammonium cations both connect to two oxygen atoms through hydrogen bonds, including one non-coordinate O atom from the Ttha ligand in the same molecule, and the other from the crystallization water molecule for N(5), two O atoms from the crystallization water molecules for N(6). While N(7) connects to five oxygen atoms through hydrogen bonds, including three non–coordinate O atoms from three neighbor Ttha ligands, and the others from the crystallization water molecules. The crystallization water molecules are coordinated as well as non-coordinate, O atom of the Ttha ligands are linked through hydrogen bonds in a unit cell. Therefore, a net structure is formed through hydrogen bonds and electrostatic actions.

In complex **III**, the central Dy^{3+} ion is eight-coordinated by a Cydta ligand and two water molecules

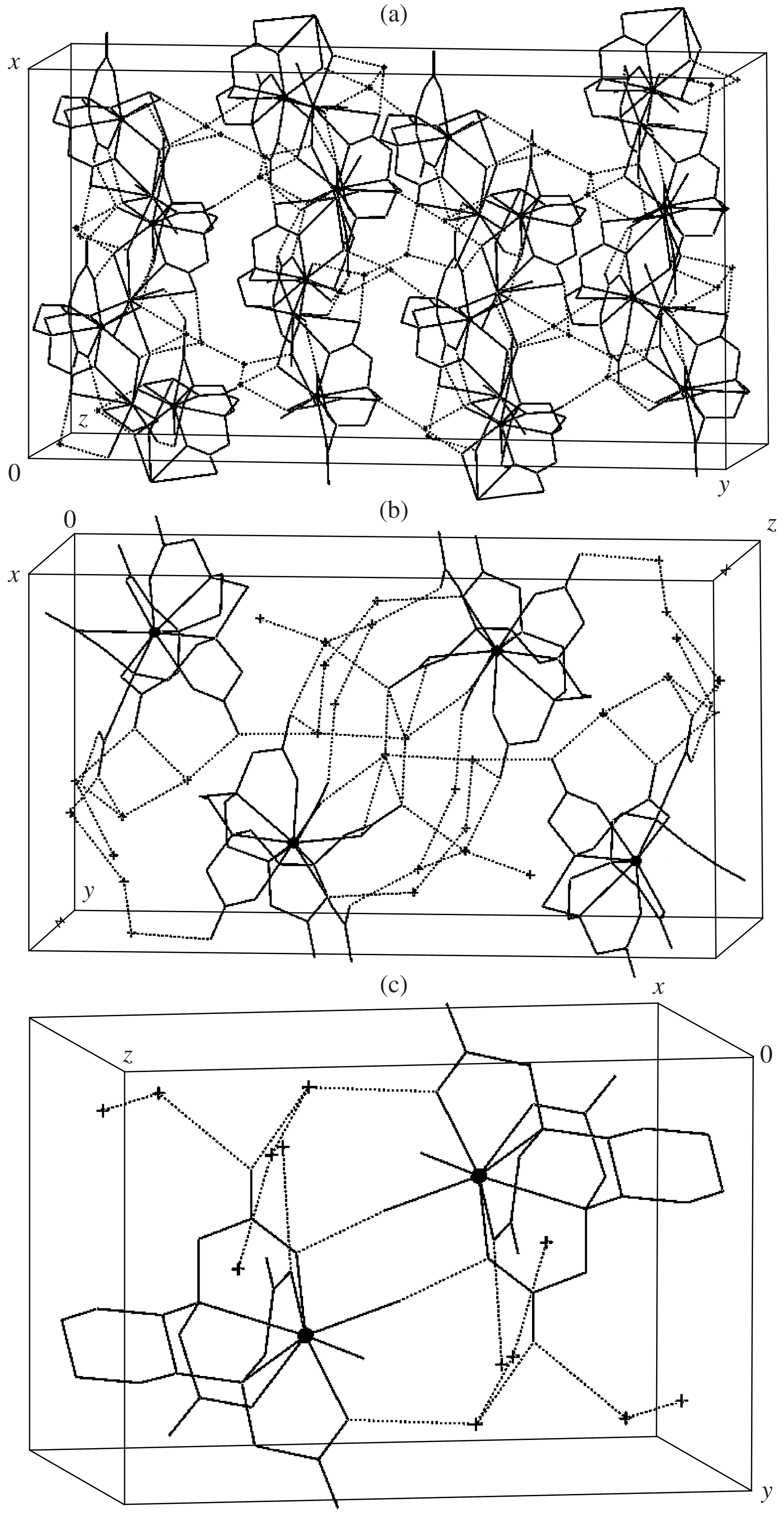

Fig. 2. Arrangement of complex **I** (a), **II** (b), and **III** (c) in unit cell (dashed lines represent intermolecular hydrogen bonds).

shown in Fig. 1c. The eight donor atoms, including four carboxyl oxygen atoms and two amine nitrogen atoms, which come from the same Cydta ligand, and two oxygen atoms from two coordinate water molecules, yield a slightly distorted square antiprismatic conformation. The average Dy–O bond distance is 2.333(6) Å, with the longest one being 2.369(6) Å (Dy–O(9)) and the shortest one being 2.311(6) Å (Dy–O(1)). The Dy–N bond distances are longer than Dy–O. The average bond distance of Dy–N is 2.563(7) Å, with the longest one being 2.564(7) Å (Dy–N(1)) and the shortest one being 2.561(6) Å (Dy–N(2)). The set of N(2), O(5), O(9), and O(7) atoms and the set of N(1), O(1), O(10), and O(3) atoms form two approximate squares, respectively. As a hexadentate ligand, each Cydta ligand coordinates to a single Dy^{3+} ion with its six donor atoms. As a result, five five-membered rings form similar to the complex **I**. Perhaps, there are two conceivable reasons for eight-coordinate structure: (1) two coordinate carboxylic groups on each N atom are affected by the cyclohexyl group with the rigidity in the Cydta ligand; (2) the alkalinities of two N atoms on cyclohexyl group in the Cydta ligand are stronger than those of two N atoms on the ethyl group in the Edta ligand. Of course, the exact reasons are need to be further studied.

As shown in Fig. 2c, the complex **III** crystallizes in the triclinic system, space group $P\bar{1}$, with two complex molecules in a unit cell. The $[Dy(Cydta)(H_2O)_2]^-$ complex anions are connected by ammonium cations and hydrogen bonds, which play very important role in stabilizing the crystal structure. As a bridge, N(3) of the ammonium cation connects three oxygen atoms through hydrogen bonds, including one non-coordinate O atom from a neighbor ligand Cydta, and the others from crystallization water molecules. The crystallization water molecules, coordinate water molecules, and coordinate, as well as non-coordinate, O atoms of the Cydta ligands are linked through hydrogen bonds in a unit cell. Here, the hydrogen bonds between coordinate water molecule and coordinate O atoms of the neighbor Cydta ligands advantage the stabilization of the crystal structure. Therefore, a net structure is formed through hydrogen bonds and electrostatic actions.

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