Asian Journal of Chemistry Vol. 21, No. 6 (2009), 4711-4720

Hydrothermal Synthesis and Crystal Structure of a Novel 3D Heteronuclear Cerium and Silver Coordination Compound

CHONG-CHEN WANG
School of Environment and Energy Engineering, Beijing University of Civil Engineering and Architecture, No. 1, Zhanlanguan Road, Xicheng District, Beijing-100044, P.R. China
E-mail: chongchenwang@126.com

The coordination compound $Ce_4Ag_2(bpdc)_4(SO_4)_3(H_2O)_6 \cdot H_2O$, where bpdc is 2,2'-bipyridine-4,4'-dicarboxylic acid, has been synthesized and its crystal structure was determined by X-ray diffraction. Crystal data: orthorhombic, space group Ama2, a = 26.990 (3) Å, b = 33.060 (3) Å, c = 6.9250(10) Å, V = 6179.1(12) $Å^3$, M_r = 2159.26, F(000) = 4144, Z = 4, D_c = 2.321 Mg/m^3, μ = 3.715 mm^{-1}. The final R_1 = 0.1468 and wR_2 = 0.3188 for 4553 observed reflections ($I>2\sigma(I)$). Silver(I) ion is coordinated by nitrogen atoms on the pyridine rings *via* chelating mode, showing the distorted tetrahedron geometry. The coordination polyhedron around Ce(1) is 8-coordinated dodecahedron mo de, while the local geometry around Ce(2) is 8-coordinated bicapped trigonal prism. The title compound is in 3-dimensional supramolecular state.

Key Words: Heteronuclear coordination compound, Cerium, Silver, Crystal structure.

INTRODUCTION

There is considerable current interest in the synthesis and characterization of multi-dimensional coordination polymers because of their applications. Polydentate ligands, which are used as building blocks in constructing the coordination polymers are quite important in the crystal engineering of the supramolecular architecture organized by coordinate covalent or hydrogen bonding interaction. 2,2'-Bipyridine-4,4'-dicarboxylic acid (bpdc) is a potential bridging ligand in various coordination models as a result of its multi-functional groups. The synthesis, structure and properties on the coordination compound constructed by bpdc and transition and lanthanide metal were investigated[1-7], which revealed that bpdc is versatile organic ligand due to its diverse coordination modes of carboxylate groups. Up to now, although some coordination polymers composing of bpdc were reported[1-7], no heteronuclear one was investigated. In this communication, the preparation and crystal structure of a novel 3D heteronuclear cerium and silver coordination compound, in which the Ag(I) ion is coordinated by nitrogen atoms on the pyridine rings *via* chelating mode, showing the distorted tetrahedron geometry is reported. The coordination polyhedron around Ce(1) is 8-coordinated dodecahedron made, while the local geometry around

Ce(2) is 8-coordinated bicapped trigonal prism. The title compound is in three-dimensional supramolecular state and the inorganic $[SO_4]^{2-}$ units show their versatile coordination mode.

EXPERIMENTAL

All reagents were of AR grade and used without further purification. Elemental analysis was performed by Elementar Vario EL-III analyzer.

Synthesis: Yellow block-like $Ce_4Ag_2(bpdc)_4(SO_4)_3(H_2O)_6 \cdot H_2O$ was obtained from hydrothermal reaction of the mixture of $Ce(NO_3)_3 \cdot 6H_2O$ (86.8 mg, 0.2 mmol), Ag_2SO_4 (62.3 mg 0.2 mmol), 2,2'-bipyridine-4,4'-dicarboxylic acid (97.6 mg, 0.4 mmol) and distilled water (13 mL, 0.722 mol) in a mole ratio of 1:1:2:3610 in 25 mL polytetrafluoroethylene-lined stainless steel reaction container at 150 ºC for 120 h. Elemental analysis (%): Calcd. for $C_{48}H_{38}N_8O_{35}S_3Ag_2Ce_4$: N 5.19, C 26.68, H 1.76, S 4.45. Found: N 5.15, C 26.85, H 1.90, S 4.16.

Crystal structure determination: A yellow single crystal (0.28 mm × 0.14 mm × 0.09 mm) was carefully selected under microscope and was mounted on a glass fiber capillary for intensity data collection on a Bruker CCD area detector diffactometer with a graphite-monochromatized MoKα radiation (λ = 0.71073 Å) from a generator operating at 50 kV and 30 mA. The intensity data were collected in the range of $1.44^{\circ} \leq \theta \leq 25.01^{\circ}$ using ϕ-ω mode at 298(2) K. A total reflections of 14035 were collected, of which 5081 reflections with $R_{int} = 0.1128$ were unique and 4553 were observed ($I>2\sigma(I)$). Empirical absorption corrections were performed with the SADABS program. The structure has been solved by direct methods (SHELXS-97)[8] and refined by full-matrix-least squares techniques on F^2 with anisotropic thermal parameters for all of the non-hydrogen atoms (SHELXL-97)[8]. All hydrogen atoms were located by Fourier difference synthesis and geometrical analysis. These hydrogen atoms were allowed to ride on their respective parent atoms. The final full-matric least-squares refinements including 472 parameters for 4553 reflections with $I > 2\sigma(I)$ gave R1 = 0.1468, wR2 = 0.3188 $\{w = 1/[\sigma^2(F_0^2) + (0.0816 (F_o^2 + 2F_c^2)/3)^2 + 0.09 (F_0^2 + 2F_c^2)/3]\}$, $(\Delta\rho)max = 6.695$ e.Å^{-3}, $(\Delta\rho)_{min} = -6.470$ e.Å^{-3}. All structural calculations were carried out using the SHELX-97 program package[8].

RESULTS AND DISCUSSION

The atomic coordinates and thermal parameters, the selected bond lengths and bond angles, anisotropic displacement parameters, hydrogen coordinates and hydrogen bonds are listed in Tables 1-5, respectively. The perspective view of the framework of title compound along c axis, the coordination mode of bpdc and silver ion, the coordination environment of cerium centers, the 2-D layer constructed from the silver and cerium centers and bpdc ligands, the role of $[SO_4]^{2-}$ anions linking the cerium centers into 1-D chain and are illustrated in Figs. 1-5, respectively.

TABLE-1
ATOMIC COORDINATES ($\times 10^4$) AND EQUIVALENT ISOTROPIC DISPLACEMENT PARAMETERS ($\times 10^3$ Å^2)

	x	y	z	U(eq)		x	y	z	U(eq)
Ce(1)	7500	9205(1)	11582(5)	18(1)	O(22)	7500	8042(14)	4570(70)	41(12)
Ce(2)	6162(1)	10025(1)	6812(4)	24(1)	S(1)	7500	10076(4)	8090(20)	20(3)
Ce(3)	7500	11089(1)	10434(4)	17(1)	S(2)	5000	10000	6870(30)	28(3)
Ag(1)	5144(1)	7371(1)	8475(8)	45(1)	S(3)	7500	12026(4)	11180(20)	24(3)
N(1)	5652(12)	7946(9)	7920(50)	23(8)	C(1)	6161(15)	7931(11)	7610(60)	23(9)
N(2)	4697(12)	7937(9)	8840(50)	24(8)	C(2)	6438(15)	8285(11)	7630(60)	24(9)
N(3)	5594(12)	6804(8)	8900(50)	23(8)	C(3)	6207(15)	8655(11)	7960(70)	24(9)
N(4)	4656(12)	6796(9)	7890(50)	22(8)	C(4)	5698(14)	8670(11)	8270(60)	24(9)
O(1)	6941(10)	8956(7)	9260(40)	24(6)	C(5)	5421(15)	8316(11)	8250(60)	24(9)
O(2)	6366(10)	9324(8)	7570(40)	25(6)	C(6)	4889(14)	8315(10)	8390(60)	23(9)
O(3)	6031(10)	10717(8)	7980(40)	26(7)	C(7)	4580(14)	8651(10)	8340(60)	23(9)
O(4)	6661(10)	11072(7)	9350(40)	24(6)	C(8)	4079(14)	8609(10)	8760(70)	23(9)
O(5)	6354(9)	10419(7)	3680(40)	25(6)	C(9)	3886(16)	8231(11)	9210(60)	24(10)
O(6)	6989(10)	10843(7)	3170(50)	26(6)	C(10)	4196(15)	7895(11)	9260(60)	24(9)
O(7)	6689(10)	9261(8)	2850(40)	26(7)	C(11)	6560(15)	9010(11)	8390(70)	24(9)
O(8)	6066(10)	9603(8)	4220(40)	24(6)	C(12)	6224(14)	11045(11)	8640(70)	24(9)
O(9)	7500	9684(10)	8670(60)	23(9)	C(13)	6104(15)	6848(11)	9070(60)	23(10)
O(10)	7064(10)	10118(7)	7140(40)	25(7)	C(14)	6411(15)	6512(10)	8900(60)	23(9)
O(11)	7500	10410(10)	9450(60)	20(8)	C(15)	6207(14)	6132(10)	8560(70)	23(9)
O(12)	5328(10)	9772(8)	7840(40)	27(7)	C(16)	5697(14)	6089(11)	8390(60)	23(9)
O(13)	5317(10)	10183(8)	4960(40)	26(7)	C(17)	5390(14)	6425(11)	8560(70)	23(8)
O(14)	7500	11813(11)	9410(60)	24(9)	C(18)	4868(14)	6423(11)	8300(60)	22(8)
O(15)	7500	11709(11)	12510(60)	22(9)	C(19)	4571(14)	6081(10)	8460(60)	23(8)
O(16)	7977(11)	12255(8)	11240(40)	29(7)	C(20)	4062(14)	6112(10)	8210(60)	22(9)
O(17)	7500	8563(11)	12420(50)	20(9)	C(21)	3849(15)	6486(10)	7800(60)	22(9)
O(18)	7500	9057(12)	15160(70)	33(10)	C(22)	4146(15)	6827(11)	7640(60)	22(9)
O(19)	7500	9891(10)	13200(60)	23(9)	C(23)	6572(15)	10787(11)	3780(70)	25(9)
O(20)	6200(11)	10020(8)	10500(50)	35(7)	C(24)	6262(14)	9280(11)	3500(70)	24(9)
O(21)	7500	11047(10)	6840(80)	31(9)					

U(eq) is defined as one third of the trace of the orthogonalized U_{ii} tensor.

TABLE-2
SELECTED BOND LENGTH (Å) AND ANGLES (º)

Ce(1)-O(17)	2.20(4)	O(17)-Ce(1)-O(1)	80.9(10)	O(12)-Ce(2)-O(5)	126.0(9)
Ce(1)-O(1)	2.35(3)	O(17)-Ce(1)-O(1)#1	80.9(10)	O(20)-Ce(2)-O(5)	146.5(9)
Ce(1)-O(1)#1	2.35(3)	O(1)-Ce(1)-O(1)#1	79.7(14)	O(8)-Ce(2)-O(13)	69.2(9)
Ce(1)-O(7)#2	2.37(3)	O(17)-Ce(1)-O(7)#2	88.7(7)	O(2)-Ce(2)-O(13)	118.8(9)
Ce(1)-O(7)#3	2.37(3)	O(1)-Ce(1)-O(7)#2	71.8(10)	O(3)-Ce(2)-O(13)	81.5(9)
Ce(1)-O(18)	2.53(5)	O(1)#1-Ce(1)-O(7)#2	50.9(10)	O(10)-Ce(2)-O(13)	149.8(9)
Ce(1)-O(19)	2.53(3)	O(17)-Ce(1)-O(7)#3	88.7(7)	O(12)-Ce(2)-O(13)	55.4(9)
Ce(1)-O(9)	2.57(4)	O(1)-Ce(1)-O(7)#3	50.9(10)	O(20)-Ce(2)-O(13)	121.0(9)
Ce(2)-O(8)	2.29(3)	O(1)#1-Ce(1)-O(7)#3	71.8(10)	O(5)-Ce(2)-O(13)	70.8(9)
Ce(2)-O(2)	2.44(3)	O(7)#2-Ce(1)-O(7)#3	35.4(14)	O(11)-Ce(3)-O(4)	83.4(7)

Ce(2)-O(3)	2.45(3)	O(17)-Ce(1)-O(18)	63.5(13)	O(11)-Ce(3)-O(4)#1	83.4(7)
Ce(2)-O(10)	2.47(3)	O(1)-Ce(1)-O(18)	127.0(9)	O(4)-Ce(3)-O(4)#1	143.1(15)
Ce(2)-O(12)	2.50(3)	O(1)#1-Ce(1)-O(18)	127.0(9)	O(11)-Ce(3)-O(6)#3	84.8(10)
Ce(2)-O(20)	2.55(3)	O(7)#2-Ce(1)-O(18)	69.6(7)	O(4)-Ce(3)-O(6)#3	139.6(10)
Ce(2)-O(5)	2.58(3)	O(7)#3-Ce(1)-O(18)	69.6(7)	O(4)#1-Ce(3)-O(6)#3	72.9(10)
Ce(2)-O(13)	2.67(3)	O(17)-Ce(1)-O(19)	138.4(13)	O(11)-Ce(3)-O(6)#2	84.8(10)
Ce(3)-O(11)	2.35(3)	O(1)-Ce(1)-O(19)	128.1(8)	O(4)-Ce(3)-O(6)#2	72.9(10)
Ce(3)-O(4)	2.39(3)	O(1)#1-Ce(1)-O(19)	128.1(8)	O(4)#1-Ce(3)-O(6)#2	139.6(10)
Ce(3)-O(4)#1	2.39(3)	O(7)#2-Ce(1)-O(19)	76.4(7)	O(6)#3-Ce(3)-O(6)#2	67.6(13)
Ce(3)-O(6)#3	2.48(3)	O(7)#3-Ce(1)-O(19)	76.4(7)	O(11)-Ce(3)-O(21)	69.8(12)
Ce(3)-O(6)#2	2.48(3)	O(18)-Ce(1)-O(19)	74.9(13)	O(4)-Ce(3)-O(21)	71.5(7)
Ce(3)-O(21)	2.50(5)	O(17)-Ce(1)-O(9)	143.4(13)	O(4)#1-Ce(3)-O(21)	71.5(7)
Ce(3)-O(14)	2.50(4)	O(1)-Ce(1)-O(9)	71.3(9)	O(6)#3-Ce(3)-O(21)	138.1(8)
Ce(3)-O(15)	2.50(4)	O(1)#1-Ce(1)-O(9)	71.3(9)	O(6)#2-Ce(3)-O(21)	138.1(8)
Ag(1)-N(2)	2.24(3)	O(7)#2-Ce(1)-O(9)	104.1(7)	O(11)-Ce(3)-O(14)	146.5(14)
Ag(1)-N(3)	2.25(3)	O(7)#3-Ce(1)-O(9)	104.1(8)	O(4)-Ce(3)-O(14)	86.1(7)
Ag(1)-N(4)	2.35(3)	O(18)-Ce(1)-O(9)	153.1(12)	O(4)#1-Ce(3)-O(14)	86.1(7)
Ag(1)-N(1)	2.38(3)	O(19)-Ce(1)-O(9)	78.2(13)	O(6)#3-Ce(3)-O(14)	122.1(9)
O(6)-Ce(3)#4	2.48(3)	O(8)-Ce(2)-O(2)	67.3(10)	O(6)#2-Ce(3)-O(14)	122.1(9)
O(7)-C(24)	1.24(5)	O(8)-Ce(2)-O(3)	144.2(10)	O(21)-Ce(3)-O(14)	76.7(13)
O(7)-Ce(1)#4	2.37(3)	O(2)-Ce(2)-O(3)	148.0(10)	O(11)-Ce(3)-O(15)	161.9(13)
O(9)-S(1)	1.36(4)	O(8)-Ce(2)-O(10)	105.0(9)	O(4)-Ce(3)-O(15)	101.6(7)
O(10)-S(1)	1.35(3)	O(2)-Ce(2)-O(10)	82.9(9)	O(4)#1-Ce(3)-O(15)	101.6(7)
O(11)-S(1)	1.45(4)	O(3)-Ce(2)-O(10)	89.8(9)	O(6)#3-Ce(3)-O(15)	80.2(10)
O(12)-S(2)	1.34(3)	O(8)-Ce(2)-O(12)	85.2(10)	O(6)#2-Ce(3)-O(15)	80.2(10)
O(13)-S(2)	1.69(3)	O(2)-Ce(2)-O(12)	79.8(9)	O(21)-Ce(3)-O(15)	128.3(12)
O(14)-S(3)	1.42(4)	O(3)-Ce(2)-O(12)	95.1(9)	O(14)-Ce(3)-O(15)	51.6(14)
O(15)-S(3)	1.40(4)	O(10)-Ce(2)-O(12)	154.7(10)	N(2)-Ag(1)-N(3)	166.0(14)
O(16)-S(3)	1.49(3)	O(8)-Ce(2)-O(20)	141.6(9)	N(2)-Ag(1)-N(4)	113.1(11)
S(1)-O(10)#1	1.35(3)	O(2)-Ce(2)-O(20)	76.7(9)	N(3)-Ag(1)-N(4)	69.6(11)
S(2)-O(12)#5	1.34(3)	O(3)-Ce(2)-O(20)	71.5(9)	N(2)-Ag(1)-N(1)	70.2(11)
S(2)-O(13)#5	1.69(3)	O(10)-Ce(2)-O(20)	82.6(10)	N(3)-Ag(1)-N(1)	112.1(10)
S(2)-Ce(2)#5	3.137(2)	O(12)-Ce(2)-O(20)	75.6(10)	(4)-Ag(1)-N(1)	160.8(13)
S(3)-O(16)#1	1.49(3)	O(8)-Ce(2)-O(5)	70.9(9)	C(1)-N(1)-C(5)	120(3)
		O(2)-Ce(2)-O(5)	127.9(9)	C(1)-N(1)-Ag(1)	124(2)
		O(3)-Ce(2)-O(5)	80.5(9)	C(5)-N(1)-Ag(1)	115(2)
		O(10)-Ce(2)-O(5)	79.4(9)	C(10)-N(2)-C(6)	120(3)

Symmetry transformations used to generate equivalent atoms: #1: -x+3/2, y, z; #2: x, y, z+1; #3: -x+3/2, y, z+1; #4 : x, y, z-1; #5: -x+1, -y+2, z; #6: x, y-1/2, z+1/2; #7: -x+1, -y+3/2, z+1/2; #8: x, y+1/2, z-1/2; #9: -x+1, -y+3/2, z-1/2.

The title compound, $Ce_4Ag_2(bpdc)_4(SO_4)_3(H_2O)_6 \cdot H_2O$, crystallizes in orthorhombic space group Ama2. The crystal structure determination reveals a new 3D framework, as shown in Fig. 1. The 3D framework of the title compound is constructed by cerium(III) ions and silver(I) ions as template, which is coordinated both by multi-dentate organic ligand 2,2'-bipyridine-4,4'-dicarboxylic acid and versatile inorganic ligand $[SO_4]^{2-}$. The coordinated water molecules and lattice water molecules also play an important role in building such novel structure *via* lots of hydrogen bonding interactions.

TABLE-3
ANISOTROPIC DISPLACEMENT PARAMETERS ($\times 10^3$ Å^2)

	U_{11}	U_{22}	U_{23}	U_{23}	U_{13}	U_{12}
Ce(1)	26(1)	8(1)	18(2)	-1(1)	0	0
Ce(2)	23(1)	14(1)	33(1)	-3(1)	-1(1)	2(1)
Ce(3)	24(2)	4(1)	24(2)	-3(1)	0	0
Ag(1)	37(2)	0(1)	97(3)	-2(2)	-1(2)	-1(1)
N(1)	31(18)	8(14)	30(20)	-4(13)	0(15)	0(13)
N(2)	32(18)	7(14)	30(20)	-3(14)	-1(16)	-1(13)
N(3)	29(17)	7(14)	30(20)	-7(14)	-8(16)	-5(13)
N(4)	28(17)	7(15)	30(20)	-7(13)	-7(15)	-6(13)
O(1)	30(15)	12(12)	30(18)	-1(12)	-3(13)	2(11)
O(2)	31(15)	12(13)	31(16)	-2(11)	-1(13)	1(11)
O(3)	31(15)	14(13)	34(18)	-3(12)	1(13)	1(11)
O(4)	30(15)	11(12)	31(18)	-4(11)	-1(13)	1(11)
O(5)	29(14)	14(12)	31(16)	-1(12)	1(13)	-1(11)
O(6)	31(15)	13(13)	33(17)	-3(12)	-3(13)	0(11)
O(7)	32(16)	15(13)	31(18)	-4(12)	-2(13)	0(12)
O(8)	30(15)	14(13)	29(17)	-3(11)	1(13)	2(11)
O(9)	30(20)	10(17)	30(20)	2(18)	0	0
O(10)	30(14)	13(12)	30(20)	-3(11)	0(13)	1(10)
O(11)	30(20)	7(16)	20(20)	-4(16)	0	0
O(12)	31(15)	18(14)	33(18)	0(12)	0(13)	3(12)
O(13)	31(15)	16(13)	30(20)	-2(12)	2(13)	1(11)
O(14)	30(20)	11(18)	30(20)	-2(16)	0	0
O(15)	30(20)	10(17)	30(20)	-2(15)	0	0
O(16)	38(16)	15(13)	34(19)	3(11)	-4(13)	-1(11)
O(17)	21(18)	21(19)	20(20)	1(16)	0	0
O(18)	40(20)	30(20)	30(30)	0(20)	0	0
O(19)	30(20)	8(17)	30(20)	-6(16)	0	0
O(20)	48(18)	17(14)	41(18)	0(16)	-4(16)	4(13)
O(21)	40(20)	16(18)	40(30)	0(20)	0	0
O(22)	40(30)	40(30)	40(30)	0(20)	0	0
S(1)	29(7)	5(6)	27(8)	-1(5)	0	0
S(2)	30(6)	15(6)	40(8)	0	0	5(6)
S(3)	33(8)	9(6)	31(9)	2(5)	0	0
C(1)	30(20)	8(17)	30(20)	-6(15)	0(18)	0(16)
C(2)	30(20)	9(17)	30(20)	-4(15)	-2(17)	0(16)
C(3)	30(20)	9(18)	30(20)	-3(16)	-1(19)	0(16)
C(4)	30(20)	9(17)	30(20)	-2(17)	-1(19)	0(15)
C(5)	30(20)	7(17)	30(20)	-4(16)	-1(19)	0(15)
C(6)	30(20)	7(16)	30(20)	-4(17)	-1(19)	0(15)
C(7)	30(20)	7(17)	30(30)	-4(16)	0(20)	1(15)
C(8)	30(20)	7(16)	30(20)	-3(16)	-1(19)	-1(15)
C(9)	30(20)	6(18)	30(30)	2(16)	0(20)	1(17)
C(10)	30(20)	7(17)	30(20)	-3(16)	-3(18)	-1(15)
C(11)	30(20)	11(17)	30(20)	-2(17)	0(20)	1(16)
C(12)	30(20)	11(18)	30(20)	-5(18)	0(20)	0(15)

	U_{11}	U_{22}	U_{23}	U_{23}	U_{13}	U_{12}
C(13)	30(20)	7(17)	30(30)	-8(16)	-8(19)	-4(16)
C(14)	30(20)	7(17)	30(20)	-7(16)	-10(18)	-5(15)
C(15)	30(20)	7(16)	30(20)	-9(17)	-8(19)	-5(15)
C(16)	30(20)	8(16)	30(20)	-6(17)	-8(19)	-5(14)
C(17)	30(20)	8(16)	30(20)	-7(16)	-10(20)	-5(15)
C(18)	30(20)	7(15)	30(20)	-8(16)	-7(18)	-6(15)
C(19)	30(20)	8(16)	30(20)	-8(17)	-6(19)	-7(15)
C(20)	30(20)	7(17)	30(20)	-7(16)	-6(18)	-6(15)
C(21)	30(20)	7(18)	30(20)	-8(16)	-6(18)	-7(15)
C(22)	30(20)	8(17)	30(20)	-9(15)	-7(18)	-6(15)
C(23)	30(20)	13(18)	30(20)	-3(18)	0(20)	-1(16)
C(24)	30(20)	13(18)	30(20)	-3(18)	-1(19)	1(16)

TABLE-4
HYDROGEN COORDINATES ($\times 10^4$) AND ISOTROPIC DISPLACEMENT PARAMETERS ($\times 10^3$ Å^2)

	x	y	z	U(eq)		x	y	z	U(eq)
H(17A)	7500	8313	12130	24	H(4)	5544	8917	8486	29
H(17B)	7500	8583	13645	24	H(7)	4709	8904	8037	28
H(18B)	7241	9141	15734	40	H(9)	3551	8203	9492	29
H(19B)	7754	9910	13920	27	H(10)	4067	7642	9564	28
H(20B)	6015	9847	11048	42	H(13)	6240	7102	9295	28
H(20C)	6157	10253	10994	42	H(14)	6752	6541	9016	27
H(21B)	7242	10932	6393	37	H(16)	5560	5835	8163	27
H(22C)	7754	7901	4846	49	H(19)	4714	5831	8736	27
H(1)	6315	7684	7391	27	H(21)	3508	6506	7632	26
H(2)	6778	8275	7420	28	H(22)	4004	7077	7366	27

TABLE-5
HYDROGEN BONDS FOR THE TITLE COMPOUND (Å AND ^{O})

D-H	d(D-H)	d(H···A)	<DHA	d(D···A)	A
O17-H17B	0.850	1.885	128.46	2.504	O18
O18-H18B	0.850	2.646	127.20	3.232	O1#2
O19-H19B	0.850	2.383	137.19	3.061	O10#3
O19-H19B	0.850	3.016	112.88	3.437	S1#2
O20-H20B	0.850	2.345	128.16	2.947	O8#2
O20-H20C	0.850	2.014	125.84	2.605	O5#2
O21-H21B	0.850	2.355	129.40	2.968	O6
O22-H22C	0.850	2.419	140.71	3.123	O16#10

Symmetry transformations used to generate equivalent atoms: #2: x, y, z+1; #3: -x+3/2, y, z+1; #10: x, y-1/2, z-1/2

The coordination tetrahedron aound Ag(I) center is considerable distorted with Ag-N bond length ranging from 2.24(3) Å to 2.38(3) Å and the bond angle of N(1)-Ag(1)-N(2), N(2)-Ag(1)-N(4), N(3)-Ag(1)-N(4) and N(1)-Ag(1)-N(3) equal to 70.2(11)º, 113.1(1)º, 69.6(11)º and 112.1(10)º, respectively, as shown in Fig. 2.

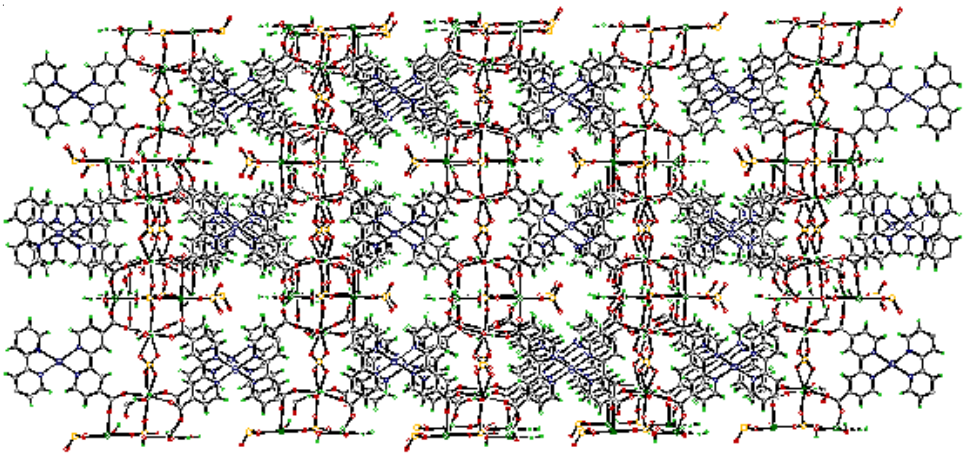

Fig. 1. Perspective view of the framework of title compound along c axis, without showing the hydrogen bonds in the structure

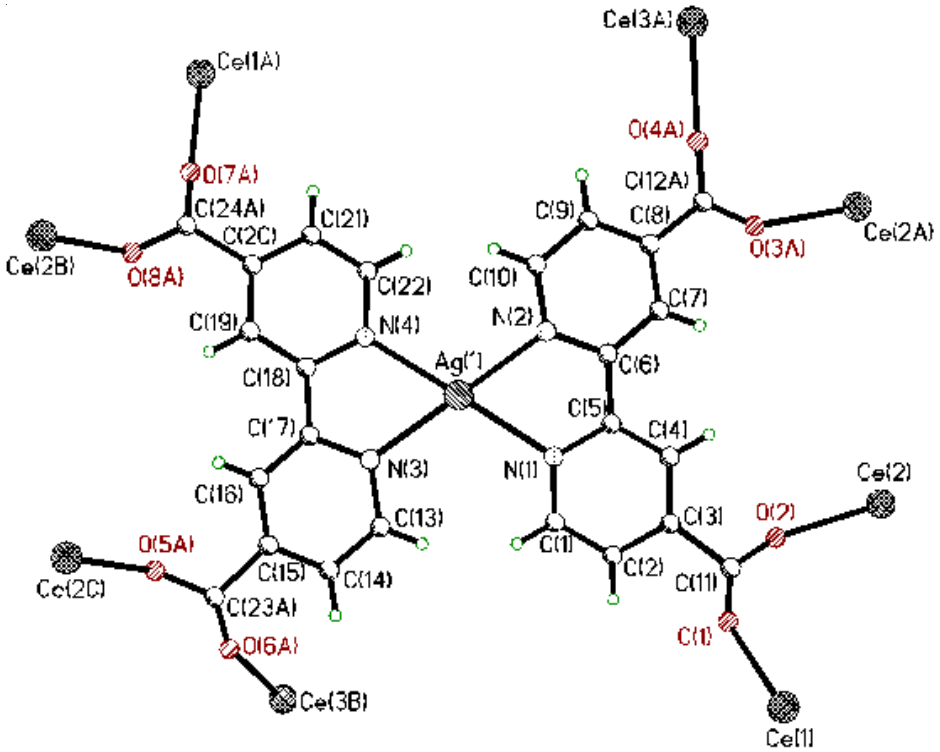

Fig. 2. Coordination mode of bpdc and Ag ion

The coordination environments around cerium ions and numbering scheme are illustrated in Fig. 3. There are two distinct cerium ions with different coordination spheres in the structure. The coordination polyhedron around Ce(1) is 8-coordinated

dodecahedron made of 4 oxygen atoms [O1, O(1A), O(7A) and O(7B)], respectively from 4 different bpdc ligands, two oxygen atoms from two $[SO_4]^{2-}$ anions and ligands and two oxygen atoms from water molecules. There are a little difference between the Ce-O_{bpdc}[2.35(3) Å and 2.37(3) Å], Ce-$O_{sulfate}$ [2.57(4) Å] and Ce-O_{water} [2.20 Å and 2.53(5) Å]. While the local geometry around Ce(2) is an 8-coordinated dicapped trigonal prism completed by 4 oxygen atoms, respectively from 4 different ligands, three oxygen atoms from two $[SO_4]^{2-}$ anions and ligands and one oxygen atom from a molecule, of which the bond distances of Ce-O_{bpdc} range from 2.29(3) Å-2.58(3) Å, Ce-$O_{sulfate}$ 2.47(3) Å - 2.67(3) Å and Ce-O_{water} 2.55(3) Å.

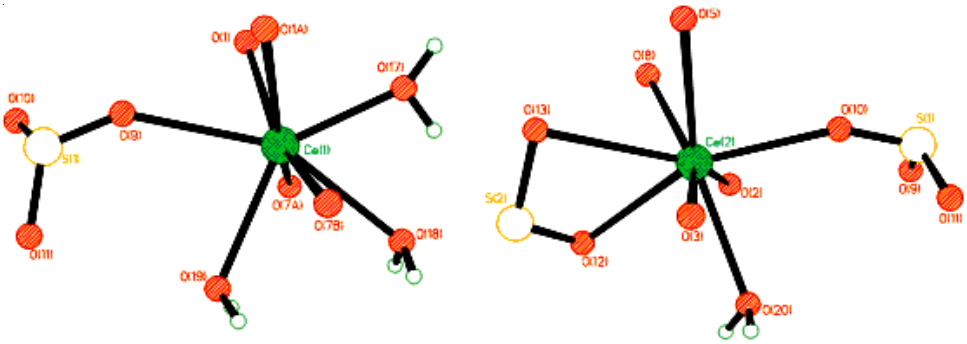

Fig. 3. The coordination environment of cerium centers

2,2'-Bipyridine-4,4'-dicarboxylic acid acts as sexadentate ligand to link silver and cerium centers into a 2-D layer along c axis (Figs. 2 and 4), in which the two N atoms on the each pyridine ring are coordinated to the same Ag atoms in chelating mode and the two O atoms of carboxylato attached on the pyridine ring are coordinated to two different Ce atoms in bis(monodentate) mode. The coordination mode of bpdc reported here can be found in the coordination compounds like Mn-bpdc[1] and Co-bpdc[5].

The $[SO_4]^{2-}$ anions play the role of inorganic ligands to link the cerium centers into 1-D inorganic chain, with different link modes (Fig. 5). Four oxygen atoms in the subunits of $[S(1)O_4]^{2-}$ join 4 different cerium center in monodentate mode, in which the S(1) shows distorted tetrahedron with S-O bond distance ranging from 1.35(3) Å to 1.45(4) Å and bond angles of O(10)-S(1)-O(9), O(10A)-S(1)-O(9), O(10)-S(1)-O(11) and O(10A)-S(1)-O(11) are 104.0(15)º, 104.0(14)º, 103.7(14)º and 103.7(14)º. Each $[S(2)O_4]^{2-}$ links two cerium centers *via* oxygen atoms in chelating mode, of which the bond distance of S(2)-O(12) [1.34(3) Å] is shorter than S(2)-O(13) [1.69(3) Å] and the bond angle of O(13)-S(2)-O(12A) [121.5(16) Å] in the $[S(2)O_4]^{2-}$ leads to a seriously distorted tetrahedron. While in the $[S(3)O_4]^{2-}$, only two oxygen atoms are coordinated to cerium centers, the other two are terminal ones. The bond distance of S-$O_{coordinated}$ [1.42 (4) Å and 1.40(Å)] is shorter than S-$O_{terminal}$ [1.49(3) Å].

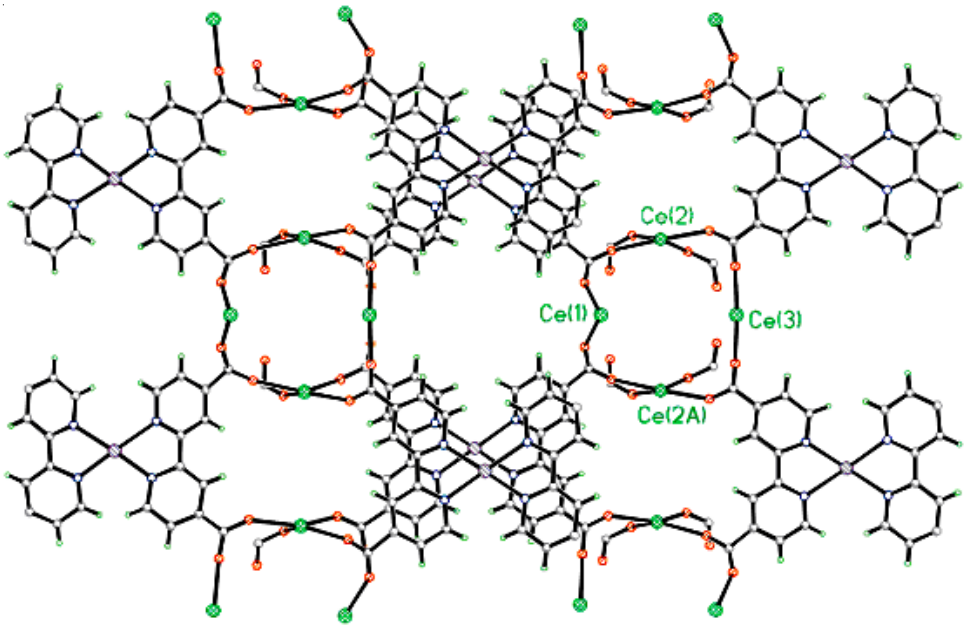

Fig. 4. 2-D layer constructed from the silver and cerium centers and bpdc ligands

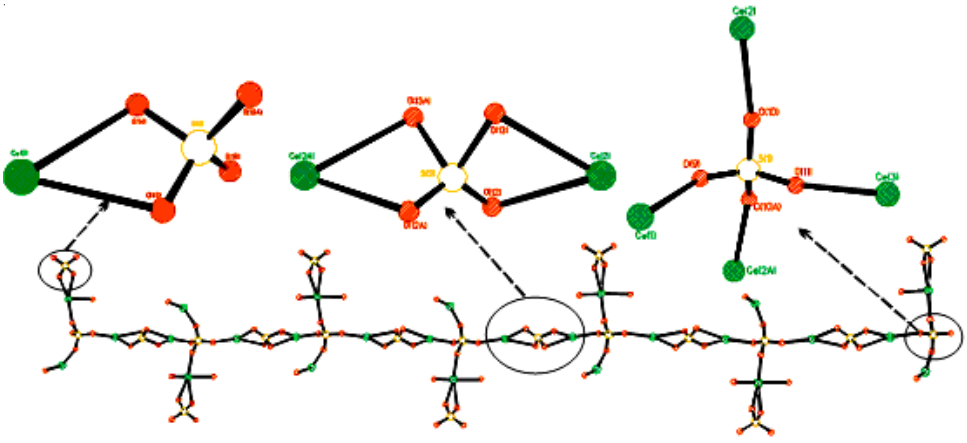

Fig. 5. Role of $[SO_4]^{2-}$ anions linking the cerium centers into 1-D chain

The hydrogen-bonding interactions from the coordinated water molecules to carboxylate oxygen atoms and sulfur atoms are observed, which also contribute to building a novel heteronuclear coordination compound (Table-5).

In conclusion, the title compound with novel 3D framework was hydrothermally synthesized, which included heteronuclear cerium and silver ions as template. The optical, magnetic and thermal properties of the title compound are in progress.

ACKNOWLEDGEMENTS

This work is financially supported by Funding Project for Academic Human Resources Development in Institutions of Higher Learning Under the Jurisdiction of Beijing Municipality(Grant no. BJE10016200611), the Research Fund of Beijing University of Civil Engineering and Architecture (grant no. 100700502).

REFERENCES

1. T. Schareina, C. Schick and R. Kempe, *Z. Anorg. Allg. Chem.*, **627**, 131 (2001).
2. T. Schareina, C. Schick, B.F. Abrahams and R. Kempe, *Z. Anorg. Allg. Chem.*, **627**, 1711 (2001).
3. E. Eskelinea, S. Luukkanen, M. Haukka, M. Ahlgren and T.A. Pakkanen, *J. Chem. Soc., Dalton Trans.*, 2745 (2000).
4. E. Tynan, P. Jensen, P.E. Kruger and A.C. Lee, *Chem. Commun.*, 776 (2004).
5. E. Tynan, P. Jensen, N.R. Kelly, P.E. Kruger and A.C. Lee, *J. Chem. Soc., Dalton Trans.*, 3440 (2004).
6. V.H. Liu, Y.L. Lu, H.C. Wu, J.C. Wang and K.L. Lu, *Inorg. Chem.*, **41**, 2592 (2002).
7. J.Y. Wu, T.T. Yeh, Y.S. Wen, J. Twu and K.L. Lu, *Cryst. Growth Des.*, **6**, 467 (2006).
8. G.M. Sheldrick, SHELXS97 and SHELXL97, University of Gottingen, Germany (1997).

(*Received*: 6 September 2008; *Accepted*: 28 March 2009) AJC-7384