双吡啶化合物3,7-di(3-pyridyl)-1,5-dioxa-3,7-diazacyclooctane 构建的四个过渡金属配合物的合成、结构及热稳定性

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摘要:采用准刚性的双吡啶化合物3,7-di(3-pyridyl)-1,5-dioxa-3,7-diazacyclooctane (L),合成了4个过渡金属配合物[Co(NO₃) (H₂O)₂(L)₂]NO₃ (1)、[Co₂Cl₄(L)₂]·CH₂Cl₂ (2)、[Cd₂(AcO)₄(L)₂]·4CH₃OH (3)和[Cd₂(NO₃)₂(CH₃OH)₂(H₂O)₂(L)₂](NO₃)₂·2H₂O (4)。单晶衍射 分析表明,配合物1是单核结构,配合物2是24-元环状双核结构,而配合物3和4为多边形双核结构。在这些配合物中,双吡啶 配体分别采用了单齿、*trans*-和*cis*-桥连3种不同配位方式。配合物经过了元素分析、红外、热重和X射线单晶结构分析表征。

关键词:钻;镉;3,7-di(3-pyridyl)-1,5-dioxa-3,7-diazacyclooctane;双吡啶;晶体结构
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Preparation, Structures and Thermal Stabilities of Four Transition Metal Complexes Constructed by 3,7-Di(3-pyridyl)-1,5-dioxa-3,7-diazacyclooctane Bipyridine Ligand

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Abstract: Four transition metal complexes, $[Co(NO_3)(H_2O)_2(L)_2]NO_3$ (1), $[Co_2Cl_4(L)_2] \cdot CH_2Cl_2$ (2), $[Cd_2(AcO)_4(L)_2] \cdot 4CH_3OH$ (3) and $[Cd_2(NO_3)_2(CH_3OH)_2(H_2O)_2(L)_2](NO_3)_2 \cdot 2H_2O$ (4), were synthesized by employing a clamplike bipyridine ligand 3,7-di(3-pyridyl)-1,5-dioxa-3,7-diazacyclooctane (L). Single-crystal X-ray analysis reveals that complex 1 is mononuclear structure; 2 is macrocyclic dimer; wheras 3 and 4 are rectangular dinuclear structures. The ligand molecules in these complexes has shown three types of coordination mode including mono-dentate, *trans*-bridge and *cis*-bridge. All of the complexes were also characterized by elemental analysis, IR, thermal stabilities and single-crystal structure analysis. CCDC: 940778, 1; 915840, 2; 1446573, 3; 1446574, 4.

Keywords: cobalt; cadmium; 3,7-di(3-pyridyl)-1,5-dioxa-3,7-diazacyclooctane; bipyridine; crystal structure

0 Introduction

Pyridine ligands have been employed extensively in constructing functional materials with transition metal^[1-13]. They have shown many advantages containing appropriate coordination capability, uncharged property, easy structural design as well as versatile coordination mode. N,N'-bidentate bipyridine has drawn much attention during these decades. Those ligands with larger spacer have been used to construct porous metallocyclic architectures, metal-organic frameworks (MOFs), optical complexes and so on, such as bis(4-(pyridine-4-yl)phenyl)amine^[3], N, N' - (1, 2 - phenylene)diisonicotinamide^[4], 3-bis(4-pyridyl) propane^[7], 1,2-dimethoxy-4,5-bis(2-pyridylethynyl)benzene^[8], 1,8-bis(4-pyridylethynyl)anthracene^[9], ((pyridinyl) - 1*H*-pyrazolyl)pyridine^[10],

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4,6-bis(4'-pyridylsulfide)dibenzofuran^[11], 4,6-bis(methylsulfanylmethyl) dibenzofuran^[11], 1, 1' - bis(4 - pyridyl) ferrocene^[13] and the others^[14-16]. To date, most of those ligands are flexible.

In our previous research, a clamplike bipyridine ligand 3,7-di(3-pyridyl)-1,5-dioxa-3,7-diazacyclooctane (L) has been synthesized. We have measured the ¹H NMR spectra of L in CDCl₃ in a range of -10 to 50 °C. Along with the change of temperature, the rotation of the N-C bonds accompany with alternate between "up, up" and "down, down" conformations in ligand would take place. The bipyridine ligand has shown quasirigid characteristics under room temperature. During the coordinating with copper salts, it acted as a cis-bridge ligand^[17]. Herein, as part of continuing studies on its coordination chemistry, we have built four transition metal complexes $[Co(NO_3)(H_2O_2(L)_2]NO_3$ (1), $[Co_2Cl_4(L)_2] \cdot CH_2Cl_2$ (2), $[Cd_2(AcO)_4(L)_2] \cdot 4CH_3OH$ (3) and $[Cd_2(NO_3)_2(CH_3OH)_2(H_2O)_2(L)_2](NO_3)_2 \cdot 2H_2O$ (4). They have shown diverse coordination chemistry. X-ray single-crystal structure analysis displays that 1 is a mononuclear complex, while 2~4 are dinuclear complexes. The ligand molecule in these complexes has exhibited three types of coordination mode including mono-dentate, trans-bridge and cis-bridge. All of these complexes have been characterized by elemental analysis, IR spectra, thermal gravity analysis and X-ray single-crystal structure analysis. The intra-/inter- molecular hydrogen interactions of these complexes have also been discussed.

1 Experimental

1.1 Reagents and instruments

The ligand L has been prepared and characterized previously^[17]. Other reagents were purchased from commercial sources and used as received without further purification. Carbon, hydrogen and nitrogen analysis were carried out by direct combustion on an EA1110-CHNSO elemental analyzer. FT-IR spectra were recorded on a Perkin Elmer Spectrum BX II spectrometer. Thermal stability analysis was measured on a PRT -1A Thermogravimetric Analyzer. Powder X-ray diffraction (PXRD) determination was performed on an X-ray diffractometer (X' Pert PRO MPOCPW 3040/60, Panalytical) with Cu $K\alpha$ radiation (λ =0.154 06 nm). The operating voltage and current were 40 kV and 40 mA, and the measurement was carried out over a 2 θ range of 5° to 50° in continuous scanning mode.

1.2 Preparation of complexes 1~4

Complex 1: To a Pyrex tube (6 mm inner diameter) was added 5.0 mL CH_2Cl_2 solution of L (1.0 mmol, 290 mg), then was slowly layed onto 5.0 mL CH_3OH solution of $Co(NO_3)_2 \cdot 6H_2O$ (1.0 mmol, 291 mg). The tube was sealed at room temperature for 4 d, and red block crystals of complex 1 were afforded. Yield: 481 mg (63% based on Co). Anal. Calcd. for $C_{28}H_{36}CoN_{10}O_{12}$ (%): C 44.04, H 4.75, N 18.34; Found(%): C 44.12, H 4.68, N 18.15. FT-IR (KBr, cm⁻¹): 3 412(m), 3 042(w), 2 963(w), 2 935(w), 2 902(w), 1 602(w), 1 578(m), 1 522 (s), 1 496(vs), 1 464(w), 1 443(w), 1 426(w), 1 369(vs), 1 309(s), 1 261(s), 1 229(vs), 1 193(m), 1 167(w), 1 136 (s), 1 058(s), 1 029(vs), 1 015(s), 991(s), 942(m), 888 (m), 828(w), 799(m), 781(w), 745(w), 696(m), 665(m), 621(w), 569(w), 487(w), 416(w).

Complex **2**: To a Pyrex tube was added 5.0 mL CH_2Cl_2 solution of L (1.0 mmol, 290 mg), then was slowly layed onto 5.0 mL CH_3CN solution of $CoCl_2$ (1.0 mmol, 130 mg). The tube was sealed at room temperature for 6 d, and blue block crystals of complex **2** were afforded. Yield: 231 mg (52% based on Co). Anal. Calcd. for $C_{29}H_{34}Cl_6Co_2N_8O_4(\%)$: C 39.17, H 3.85, N 12.60; Found(%): C 40.12, H 3.97, N 12.95. FT - IR (KBr, cm⁻¹): 3 413(w), 3 112(w), 3 077(w), 3 048(w), 2 980(w), 2 940(w), 2 903(w), 1 600(s), 1 577(s), 1 495 (vs), 1 438(s), 1 368(vs), 1 305(s), 1 258(m), 1 223(s), 1 197(m), 1 171(w), 1 136(s), 1 063(s), 1 038(vs), 1 015 (s), 991(s), 944(s), 889(m), 807(s), 730(m), 692(s), 663 (s), 620(w), 568(w), 496(w), 419(w).

Complex 3: It was prepared as the method for complexes 1 and 2 except that 5.0 mL CH₃OH solution of Cd(AcO)₂·2H₂O (1.0 mmol, 267 mg) was used. The tube was sealed at room temperature for 5 d, and colorless block crystals of complex 3 were afforded. Yield: 329 mg (58% based on Cd). Anal. Calcd. for C₄₀H₆₀Cd₂N₈O₁₆(%): C 42.37, H 5.33, N 9.88; Found (%): C 42.12, H 5.08, N 9.70. FT-IR (KBr, cm⁻¹): 3 440 (vs), 2 967(w), 2 963(w), 2 933(w), 1 560(vs), 1 498(s), 1 420(s), 1 364(s), 1 306(s), 1 261(m), 1 231(s), 1 199
(w), 1 166(w), 1 134(s), 1 063(s), 1 033(vs), 1 016(s), 995(s), 942(s), 876(m), 803(m), 790(w), 697(m), 670
(m),), 642(w), 620(w).

Complex 4: It was prepared the method for $1\sim3$ except that 5.0 mL CH₃OH solution of Cd(NO₃)₂·4H₂O (1.0 mmol, 308 mg) was used. After one week, colorless block crystals of complex 4 were afforded. Yield: 830 mg (72% based on Cd). Anal. Calcd. for C₃₀H₄₈Cd₂N₁₂O₂₂ (%): C 31.23, H 4.19, N 14.57; Found(%): C 31.12, H 4.02, N 14.30. FT-IR (KBr, cm⁻¹): 3 450(vs), 2 901(w), 1 602(m), 1 498(m), 1 384(vs), 1 305(s), 1 261(m), 1 233(s), 1 198(m), 1 167(w), 1 135(m), 1 062(m), 1 033 (s), 997(m), 942(m), 900(w), 881(w), 799(m), 692(m), 641(w).

1.3 Crystallographic analyses

The single crystals with dimensions of 0.50 mm× 0.40 mm×0.35 mm (1), 0.25 mm×0.22 mm×0.20 mm (2), 0.35 mm×0.25 mm×0.22 mm (3) and 0.40 mm× 0.20 mm×0.20 mm (4) were mounted on a glass fiber, relatively. Single-crystal X-ray diffraction measurements were performed on a Bruker APEX II 4K CCD area detector equipped with a graphite monochromated Mo K α radiation (λ =0.071 073 nm) by using the ω scan mode on all observed reflections in a θ range of 3.06°~25.35° (1), 3.07°~26.00° (2), 3.05°~25.02° (3) and $3.16^{\circ} \sim 24.24^{\circ}$ (4). All absorption corrections were applied using the SADABS program^[18]. The structures were solved by direct methods and refined on F^2 by full -matrix least-squares using the SHELXTL-97 program package^[19]. Metal atoms were located from the e-maps, and other non-hydrogen atoms were derived from the successive difference Fourier peaks. The nitrate anion was disordered about a twofold rotation axis in complex 4^[20]. Hydrogen atoms were placed in geometrically idealized positions (C-H 0.095~0.098 nm) and were constrained to ride on their parent atoms with $U_{iso}(H)=1.2$ ~ $1.5U_{eq}(C)$. Summary of the crystallographic data for $1\sim4$ are given in Table 1. Selected bond lengths and angles are given in Table 2. Hydrogen bonds geometries are listed in Table 3.

CCDC: 940778, **1**; 915840, **2**; 1446573, **3**; 1446574, **4**.

Complex	1	2	3	4
Empirical formula	$\rm C_{28}H_{36}CoN_{10}O_{12}$	$\mathrm{C}_{29}\mathrm{H}_{34}\mathrm{Cl}_{6}\mathrm{Co}_{2}\mathrm{N}_{8}\mathrm{O}_{4}$	$\rm C_{40}H_{60}Cd_2N_8O_{16}$	$\rm C_{30}H_{48}Cd_2N_{12}O_{22}$
Formula weight	763.60	889.20	1 133.76	1 153.60
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	P2/c	C2/c	$P\overline{1}$	$P\overline{1}$
<i>a /</i> nm	1.072 8(2)	0.955 91(5)	0.958 04(4)	0.937 13(19)
<i>b</i> / nm	0.866 88(17)	2.753 00(14)	1.165 02(5)	1.070 0(2)
<i>c</i> / nm	1.870 9(6)	1.406 73(8)	1.203 89(4)	1.270 2(3)
α / (°)			107.496(3)	109.52(3)
β / (°)	108.80(3)	105.324(5)	106.103(3)	108.64(3)
γ / (°)			100.170(3)	99.59(3)
V / nm^3	1.647 1(7)	3.570 4(3)	1.180 67(8)	1.082 8(4)
Ζ	2	4	1	1
$D_{\rm c} /({\rm g}{f \cdot}{ m cm}^{-3})$	1.540	1.654	1.595	1.769
<i>F</i> (000)	794	1 808	580	584
μ / mm ⁻¹	0.600	1.426	0.977	1.079
heta range / (°)	3.06~25.35	3.07~26.00	3.05~25.02	3.16~25.00
Limiting indices	$-10 \leq h \leq 12$	$-11 \leq h \leq 11$	$-11 \leq h \leq 11$	$-10 \leq h \leq 10$
	$-10 \leq k \leq 10$	$-33 \leq k \leq 26$	$-12 \leq k \leq 13$	$-12 \leq k \leq 12$
	$-22 \leq l \leq 21$	$-12 \leq l \leq 17$	$-14 \leq l \leq 14$	$-14 \leq l \leq 14$
Total reflection	15 226	8 321	11 193	8 377

 Table 1
 Crystallographic and structural refinement details for 1~4

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Continued Table 1								
Data, restraint, parameter	3 024,	0, 305		3 506,	0, 222		4 175, 3, 302	3 392, 29, 383
Initial <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0$)34 8,		$R_1 = 0.0$	33 0,		R ₁ =0.025 1,	R ₁ =0.052 9,
	$wR_2=0$	0.074 2		wR ₂ =0	.069 5		wR_2 =0.059 2	wR ₂ =0.121 2
<i>R</i> indices (all data)	$R_1 = 0.0$)39 6,		$R_1 = 0.0$	44 5,		R ₁ =0.028 9,	R ₁ =0.062 7,
	$wR_2=0$	0.076 5		wR ₂ =0	.074 4		wR ₂ =0.061 4	wR ₂ =0.132 1
Goodness-of-fit	1.095			1.022			1.069	1.063
Largest diff. peak and hole / $(\rm e \cdot nm^{-3})$	210, -	275		289, -	325		446, -410	539, -767

Table 2	Selected bond	lengths (nm) and angles (^c	^o) for complexes 1~4
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Complex 1							
Co(1)—O(7)	0.210 28(17)	Co(1)-O(7)#1	0.210 28(17)	Co(1)-N(1)	0.211 21(16)		
Co(1)-N(1)#1	0.211 21(16)	Co(1)—O(3)	0.214 00(15)	Co(1)-O(3)#1	0.214 00(15)		
O(7)—Co(1)—O(7)#1	172.06(10)	O(7)—Co(1)—N(1)	93.67(7)	O(7)#1—Co(1)—N(1)	91.79(6)		
O(7)—Co(1)—N(1)#1	91.79(6)	O(7)#1—Co(1)—N(1)#1	93.67(7)	N(1)—Co(1)—N(1)#1	93.23(9)		
O(7)—Co(1)—O(3)	88.45(7)	O(7)#1—Co(1)—O(3)	84.67(7)	N(1)-Co(1)-O(3)	103.40(6)		
N(1)#1—Co(1)—O(3)	163.32(6)	O(7)—Co(1)—O(3)#1	84.67(7)	O(7)#1-Co(1)-O(3)#1	88.45(7)		
N(1)-Co(1)-O(3)#1	163.32(6)	N(1)#1—Co(1)—O(3)#1	103.40(6)	O(3)—Co(1)—O(3)#1	60.01(8)		
		Complex	2				
Co(1)-N(1)	0.204 42(19)	Co(1)—N(2)	0.202 1(2)	Co(1)—Cl(1)	0.223 38(7)		
Co(1)—Cl(2)	0.223 74(6)						
N(1)-Co(1)-Cl(1)	105.13(6)	N(2)—Co(1)—N(1)	107.60(8)	N(1)-Co(1)-Cl(2)	108.56(6)		
N(2)—Co(1)—Cl(1)	107.40(6)	N(2)—Co(1)—Cl(2)	107.46(5)	Cl(1)—Co(1)—Cl(2)	120.12(3)		
		Complex	3				
Cd(1)—N(2)#1	0.230(2)	Cd(1)—N(1)	0.232(2)	Cd(1)—O(3)	0.243(2)		
Cd(1)—O(4)	0.237(2)	Cd(1)—O(5)	0.243(2)	Cd(1)—O(6)	0.236(2)		
Cd(1)—O(6)#1	0.248(2)						
N(2)#1— $Cd(1)$ — $N(1)$	173.9(8)	N(2)#1— $Cd(1)$ — $O(6)$	89.2(7)	N(1)-Cd(1)-O(6)	87.0(7)		
N(2)#1— $Cd(1)$ — $O(4)$	91.4(7)	N(1)-Cd(1)-O(4)	89.3(7)	O(6)—Cd(1)—O(4)	146.9(7)		
N(2)#1— $Cd(1)$ — $O(5)$	88.0(7)	N(1)— $Cd(1)$ — $O(5)$	87.4(7)	O(6)— $Cd(1)$ — $O(5)$	92.4(7)		
O(4)— $Cd(1)$ — $O(5)$	54.6(7)	N(2)#1-Cd(1)-O(3)	91.7(7)	N(1)-Cd(1)-O(3)	94.3(8)		
O(6)—Cd(1)—O(3)	123.7(7)	O(4)— $Cd(1)$ — $O(3)$	89.4(7)	O(5)— $Cd(1)$ — $O(3)$	143.9(7)		
N(2)#1—Cd(1)—O(6)#1	94.4(7)	N(1)-Cd(1)-O(6)#1	88.9(7)	O(6)—Cd(1)—O(6)#1	71.2(8)		
O(4)— $Cd(1)$ — $O(6)$ #1	141.6(7)	O(5)— $Cd(1)$ — $O(6)$ #1	163.3(7)	O(3)—Cd(1)—O(6)#1	52.6(6)		
		Complex	4				
Cd(1)—N(2)	0.225 4(5)	Cd(1)—N(3)	0.225 4(5)	Cd(1)—O(1)	0.246 0(5)		
Cd(1)—O(1)#1	0.244 7(5)	Cd(1)—O(5)	0.235 8(6)	Cd(1)—O(7)	0.234 4(5)		
N(2)-Cd(1)-N(3)	176.53(17)	N(2)—Cd(1)—O(5)	93.05(19)	N(3)—Cd(1)—O(5)	90.49(17)		
N(2)-Cd(1)-O(4)	88.0(2)	N(3)-Cd(1)-O(4)	92.0(2)	O(5)—Cd(1)—O(4)	87.5(3)		
N(2)-Cd(1)-O(1)#1	88.07(17)	N(3)—Cd(1)—O(1)#1	90.78(17)	O(5)—Cd(1)—O(1)#1	112.9(2)		
O(4)-Cd(1)-O(1)#1	159.4(2)	N(2)—Cd(1)—O(1)	89.25(17)	N(3)—Cd(1)—O(1)	87.30(17)		
O(5)—Cd(1)—O(1)	177.3(2)	O(4)—Cd(1)—O(1)	94.1(2)	O(1)#1—Cd(1)—O(1)	65.6(2)		

Symmetry codes: #1: -x, y, -z+1/2 for 1; #1: -x+2, -y, -z+1 for 3; #1 -x+1, -y+1, -z+2 for 4.

Table 3Hydrogen bond geometries for complexes 1~4

	• 8	8	1	
D—H····A	<i>d</i> (D—H) / nm	$d(\mathbf{H}\cdots\mathbf{A})$ / nm	$d(\mathbf{D}\cdots\mathbf{A})$ / nm	$\angle D$ —H····A / (°)
Complex 1				
O(7)—H(7a)····O(5)#3	0.079	0.203	0.281 52	175
O(7)— $H(7b)$ ···· $N(2)#3$	0.091	0.183	0.273 98	176
C(1)—H(1)····O(7)#1	0.095	0.257	0.313 76	118
C(9)—H(9)····O(5)#4	0.097	0.248	0.326 90	138
C(12)—H(12A)····O(1)#5	0.097	0.252	0.335 89	144
C(14)—H(14B)····O(3)#6	0.099	0.247	0.314 70	125
Complex 2				
C(11)—H(11A)····Cl(2)#3	0.097	0.278	0.361 28	145
C(12)—H(12B)····Cl(1)#4	0.097	0.283	0.364 75	143
Complex 3				
C(1)—H(1)····O(2)	0.093	0.247	0.297 37	114
C(6)— $H(6)$ ···· $O(2)$	0.093	0.251	0.307 62	119
C(12)— $H(12B)$ ···· $O(4)$ #2	0.097	0.258	0.344 48	149
C(13)—H(13B)····O(8)#3	0.097	0.243	0.338 69	170
C(16)—H(16B)····O(1)#4	0.096	0.259	0.349 20	157
C(16)—H(16C)····O(1)#5	0.096	0.250	0.338 50	153
Complex 4				
O(4)— $H(5')$ ···· $O(2)$	0.072	0.248	0.304 3	136
O(4)— $H(5')$ ···· $O(11A)$	0.072	0.247	0.281	111
O(15)—H(15A)····O(11A)	0.096	0.206	0.274 6	127.1
O(5)— $H(2')$ ···· $O(3)$ #1	0.074	0.257	0.309 0	128.7
O(5)— $H(2')$ ···· $O(8A)$ #2	0.074	0.244	0.279 8	111.5
O(12)—H(3')····O(7)#4	0.085	0.233	0.303 1	140
O(12)—H(3')····O(11A)#5	0.085	0.259	0.317	127
O(12)—H(4')····O(5)#5	0.085	0.204	0.271 7	136
O(4)—H(5')····O(10)#3	0.072	0.214	0.274 1	142
C(1)—H(1)····O(3)#1	0.101	0.256	0.341 0	142
C(1)—H(1)····O(6)#1	0.101	0.249	0.298 8	110
C(13)—H(12)····O(8A)#2	0.095	0.255	0.318 6	124
C(13)—H(13A)····O(10)#3	0.093	0.250	0.342 5	175
C(13)—H(13B)····O(8A)#6	0.111	0.220	0.326 5	160

Symmetry codes: #1: -*x*, *y*, -*z*+1/2; #3: -*x*, *y*-1, -*z*+1/2; #4: *x*, *y*-1, *z*; #5: -*x*+1, -*y*, -*z*+1; #6: -*x*, -*y*, -*z*+1 for **1**; #3: -*x*+1, -*y*, -*z*+1; #4: -*x*+1/2, -*y*+1/2, -*z*+1 for **2**; #1: -*x*+2, -*y*, -*z*+1; #2: *x*, *y*+1, *z*; #3: -*x*+1, -*y*+1, -*z*; #4: -*x*+2, -*y*, -*z*; #5: *x*, *y*-1, *z* for **3**; #1: 1-*x*, 1-*y*, 2-*z*; #2: 1-*x*, -*y*, 1-*z*; #3: -*x*, 1-*y*, 1-*z*; #4: *x*-1, *y*, *z*; #5: *x*, 1+*y*, *z*; #6: 1-*x*, 1-*y*, 1-*z* for **4**.

2 Results and discussions

2.1 Description of crystal structures

2.1.1 Crystal structure of complex 1

Single crystal structure reveals that **1** crystallizes in the monoclinic space group P2/c. The asymmetric unit consists of a discrete $[Co(NO_3)(H_2O)_2(L)_2]^+$ cation and a free nitrate anion (Fig. 1a). In the coordination unit, the Co center adopts slightly distorted tetragonal biyramid geometry. Two molecules of water occupy the apical sites, and two pyridine nitrogen atoms (from two molecules of ligands) and a chelating nitrate anion are at the ecuatorial plane. Two molecules of L choose a mono-dentated coordination mode in the cation. They lie on the reverse side to avoid steric hindrance. On the equatorial plane, the maximum deviation of Co atom from the mean plane constructed by N1, N1A, O3 and O3A is 0.021 nm. The bite angle of N1—Co1—N1A is

93.23(9)°. It is wider than that of O3—Co1—O3A (60.01(8)°). The average bond lengths for Co—N and Co—O are 0.203 nm and 0.212 nm, separately. They are close with those in $[Co(L^1) (L^2) (H_2O)_2] \cdot 3H_2O$ (L¹= terephthalic acid; L²=2, 2' - dipyridylamine) of 0.207 and 0.214 nm, respectively^[21]. The free nitrate anion is stabilized by multiple hydrogen interactions including O…H—C (0.314~0.336 nm) and O…H—O (0.282 nm), as is shown in Fig.1b.



Fig.1 (a) Coordination structural unit with 30% probability ellipsoids in complex 1, where H atoms are omitted for clarify and the symmetry code is #1: -x, y, 1/2-z;
(b) Interactions of nitrate anion in complex 1 where the symmetry code is #1: -1+x, -1+y, z

2.1.2 Crystal structure of complex 2

Complex **2** crystallizes in the monoclinic space group C2/c. The asymmetric unit consists of a neutral $[Co(L)Cl_2]$ unit and half a CH_2Cl_2 solvent molecule, as shown in Fig.2a. In the coordination unit, each Co atom is coordinated by two nitrogen atoms from pyridine rings and two Cl atoms, adopting a tetrahedral $[CoN_2Cl_2]$ coordination geometry. The angle of N2— Co1—N1 is 107.60(8)°. It is smaller than that reported in $[Co_2Cl_4(L^3)_2]$ (L³=1,2-dimethoxy-4,5-bis(2-pyridylethynyl)benzene) of 117.53(9)°^[8]. This might be due to the tension of octagonal ring in ligand. Two pyridine rings in ligand L arrange in an opposite direction. Ligand L acts as a *trans*-bridge, and they wrap around two cobalt atoms producing a helical 24-membered macrocycle. The Co···Co distance is 0.700 nm. The distance between the center of heterooctane is 1.019 nm. The average bond lengths for Co—N (0.203 nm) and Co—Cl (0.224 nm) are in agreement with those in $[Co_2Cl_4(L^4)_2]$ (L⁴=N, N' - (1, 2 - phenylene)diisonicotinamide) (Co—N 0.203 nm, Co—Cl 0.223 nm)^[4] and $[Co_2Cl_4(L^3)_2]$ (Co—N 0.203 nm, Co—Cl 0.224 nm)



Fig.2 (a) Coordination structural unit with 30% probability ellipsoids in complex 2, where H atoms and solvent molecule are omitted for clarify; (b) Interactions of CH₂Cl₂ solvent molecule in complex 2, where the symmetry codes are #1: -x+1, -y, -z+1; #2: 1/2-x, 1/2-y, 1-z; #3: -1/2+x, 1/2-y, 1/2+z

^[8]. The free solvent molecule CH_2Cl_2 is not eclipsed in the macrocycle, and it is stabilized by three adjacent coordination molecules as is illustrated in Fig. 2b. It might result from the gentle reaction condition as well as the intermolecular hydrogen interactions of $Cl\cdots H$ — C ($Cl\cdots C$ 0.305 nm) and $O\cdots H$ —C ($O\cdots C$ 0.277 nm). 2.1.3 Crystal structure of complex **3**

Complex **3** crystallizes in the triclinic space group $P\overline{1}$. The asymmetric unit consists of a discrete [Cd(L)(μ - OAc)(OAc)] (Fig. 3a) and two molecules of methanol. The Cd center is seven - coordinated by two separate pyridine ligands, two bridged acetates and another chelated acetate anion forming a distorted pentagonal bipy-



Fig.3 (a) Coordination structural unit with 30% probability ellipsoids in complex 3, where H atoms and solvent molecules are omitted for clarify and the symmetry code is #1: 2-x, -y, 1-z; (b) Interactions of CH₃OH solvent molecules in complex 3, where the symmetry code is #1: 1-x, 1-y, 1-z

ramidal geometry. The N atoms of the bipyridine occupy the apical sites and the O atoms of the acetate units lie in the equatorial plane. In complex **3**, pyridine rings in ligand L arrange parallel to each other. Two molecules of ligand L act as *cis*-bridge, and link with two Cd $(NO_3)_2$ units forming two rectangle cavities. The Cd… Cd separation is 0.393 nm. The mean Cd—N (0.231 nm) and Cd—O (0.241 nm) bond lengths are in agreement with those in $[Cd_2(L^5)_4(L^6)_2]$ (L⁵=bis(4-bromobenzoate), L⁶=1,3-bis(4-pyridyl)propane) (0.231, 0.242 nm) ^[22]. Four free methanol molecules are stabilized by multiple hydrogen interactions of O…H—O (O…O 0.271~ 0.273 nm) and O…H—C (O…C 0.297~0.349 nm, Fig.3b).

2.1.4 Crystal structure of complex 4

Complex 4 crystallizes in the triclinic space group $P\overline{1}$. The asymmetric unit consists of a $[Cd(L)(\mu - NO_3)(CH_3OH)(H_2O)]^+$ cation (Fig.4a), one disordered nitrate anion and one molecule of water. The Cd center is six-coordinated by two separate pyridine ligands, two bridged nitrate anions, one water molecule and one methanol molecule forming a distorted tetragonal bipy-ramidal geometry. The bipyridine ligand L in complex



Fig.4 (a) Coordination structural unit with 30% probability ellipsoids in complex 4, where H atoms, counter nitrate anions and solvent molecules are omitted for clarify and the symmetry code is #1: -x+1, y, -z+1/2; (b) Hydrogen bond interactions in complex 4

4 adopts a similar coordination mode with that in complex **3**. The Cd···Cd separation is 0.412 nm. The average bond lengths for Cd—N and Cd— $O_{nitrate}$ are 0.226 and 0.246 nm, separately. They are comparable to those reported in complexes [Fe(η^5 -C₅H₄-1-C₅H₄N)₂]₂Cd₂ (NO₃)₄·CH₃OH·0.5C₆H₆ (0.224 and 0.249 nm)^[23] and [Cd₄(L⁷)₄(NO₃)₆(MeOH)₆]²⁺ (L⁷=4, 4'-bis(4-pyridyl)biphenyl) (0.226 and 0.249 nm)^[13]. One water molecule and a disordered nitrate anion are stabilized by multiple hydrogen interactions of O····H—O (O···O 0.272~

0.317 nm) and O····H—C (O···C 0.299~0.341 nm) (Fig.4b).

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In complexes $1\sim4$, the average torsion angles of two pyridyl rings varied from 42.88° (2) to 19.34° (4). The corresponding centre distances of two pyridyl rings range from 0.497 9(2) to 0.382 0 nm (4) (Table 4). Through rotation of the N—C bonds and broaden or compress of two pyridine rings, the ligand L molecule has displayed considerable flexibility to adjust itself to adapt different coordination environment.

 Table 4
 Torsion angles and centre distances between two pyridyl rings of ligand L in complexes 1~4

Compound	$L^{[17]}$	1	2	3	4
Torsion angle between two pyridyl rings / (°)	45.77	40.52	42.88	22.43	19.34
Centre distance between two pyridyl rings / nm	0.494 2	0.467 3	0.497 9	0.386 6	0.382 0

2.2 IR spectra of complexes 1 to 4

In the IR spectra of complexes $1 \sim 4$ (Fig.5), bands around 1 602, 1 578, 1 495 cm⁻¹ (1), 1 600, 1 577, 1 495 cm⁻¹ (2), 1 560, 1 498, 1 420 cm⁻¹ (3) and 1 602, 1 578, 1 499 cm⁻¹ (4) are assigned to the stretching vibrations of pyridine groups, separately. The strong peaks around 1 136 cm⁻¹ in all complexes are attributed to the stretching vibrations of the C—O—C bond. The symmetric and antisymmetric stretchings of C—H bonds (—CH₂— units in ligand) in complexes $1 \sim$ 4 are also in agreement with each other. They were in the region of 2 902~3 042 cm⁻¹ (1), 2 903~3 077 cm⁻¹ (2), 2 901~2 967 cm⁻¹ (3) and 2 901~2 974 cm⁻¹ (4), respectively. Strong vibrations of 1 370, 1 309 cm⁻¹ (1) and 1 364, 1 303 cm⁻¹ (4) are attributed to the NO₃⁻¹ anions^[24]. The isolated peak of 731 cm⁻¹ in complex 2 is



Fig.5 IR spectra of complexes 1~4

assigned as antisymmetric stretching of C—Cl bonds in $CH_2Cl_2^{[25]}$. The broad bands at 3 440 cm⁻¹ (**3**) and 3 408 cm⁻¹ (**4**) are attributed the stretching of O—H. The infrared spectra of these complexes are in good accordance with their structural features.

2.3 Thermal stabilities of L and complexes 1~4

Thermogravimetric analyses (TGA) of ligand L and complexes $1\sim4$ were carried out under air atmosphere from 30 to 700 °C with a heating rate of 10 °C • min⁻¹ using crystalline samples, and the resulting curves are shown in Fig.6. The skeleton of ligand L decomposed at around 194 °C. Correspondingly, curves in 1 (178 °C), 2 (174 °C), 3 (214 °C) and 4 (207 °C) have shown dramatic stages of weight loss, which might be attributed to the decomposition of ligand. In complex 1, the fisrt stage of weight loss (150~178 °C) is attributed



Fig.6 TGA curves of L and complexes 1~4 in air

to the loss of HNO₃ and H₂O (Obsd. 15.66%, Calcd. 16.51%), then accompanied by the degradation of ligand gradually. There are two steps of weight loss (in the region of 178~300 °C and 400~500 °C, respectively), the decomposition residue is in accordance with CoO (Obsd. 10.36%, Calcd. 9.81%). For complex 2, dichloromethane was unstable and escaped when exposing to the air, it was removed before thermogravimetric test. Ligand L molecules started to degrade at 174 °C, and it showed two complicated degradation process (in the region of 174~200 °C and 200~375 °C, separately). The final decompsition residue is suggested to be CoO (Obsd. 17.54%, Calcd. 18.13%). For complex 3, molecules of free methanol were unstable and partially escaped when exposing to the air. The weight loss of the first stage (from 30 to 105 $^{\circ}$ C) corresponds to the loss of methanol molecules (Obsd. 7.6%, Calcd. 11.3%). The weight loss of the second stage (214~700 °C) indicates the decomposition of two molecules of ligand L and CH_3COO^- . For complex 4, the weight loss of the first stage (from 30 to 100 $^{\circ}$ C) corresponds to the loss of free water molecules and methanol (Obsd. 8.54%, Calcd. 8.68%). The skeleton of ligand L began to decompose at 207 °C, and did not end up to 550 °C, exhibiting two weight loss platforms in TGA curve. Accompanied by gradually sublimation of CdO, there was almost no residue for complexes 3 and 4. Thermogravimetric analysis indicates that, the bipyridine ligands have shown obvious two steps decomposition in complexes 1, 2 and 4, and the ligands in *cis*-bridge complexes are more stable than those in mono-dentated and trans-bridge complexes.



Fig.7 PXRD patterns of complex 1

2.4 Powder X-ray diffraction of complex 1

The phase purity of bulk products of complex **1** was further confirmed by elemental analysis and PXRD. As is illustrated in Fig.7, the PXRD pattern of the synthesized sample was consistent with the simulated one from single crystal structure.

3 Conclusions

Four transition metal complexes were prepared by utility of a clamplike bipyridine ligand 3,7-di(3-pyridyl) -1,5-dioxa-3,7-diazacyclooctane. Single-crystal structures, IR spectra and thermal stabilities of these complexes have been discussed. The bipyridine ligand molecule has displayed diversity coordination mode in these complexes. All of these architectures have shown considerable stabilities. The study on its coordination chemistry with other metal ions is continuing.

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