Electronic Supplementary Information (ESI) for RSC Advances

Two Novel Isomeric Organic Anion-Water aggregations: 1D Tape and 3D 2-fold Interpenetrated Diamond Network

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Content

(1) Experiment details

Materials and General Methods.

All chemicals and solvents used in the syntheses were of analytical grade and used without further purification. Elemental analyses (C, H, N) were obtained on a Perkin-Elmer 240 elemental analyzer. Thermal gravimetric analysis (TGA) was performed under N_2 on a Perkin Elmer TGA 7 instrument.

(2) Synthesis of 1 and 2

Synthesis of {[Co(2,2'-bpy)$_3$][(imdn)$_2$(H$_2$O)$_4$]}. (1)

Mixture of $Co(NO_3)_2 \cdot 6H_2O$ (30 mg, 0.10 mmol), Himdn (15 mg, 0.13 mmol) and tetrabutyl ammonium bromide (5 mg, 0.016 mmol) was dissolved in 5 mL water, which was added into the cuvette containing 2,2'-bpy (30 mg, 0.19 mmol) in the bottom. The mixtures were capped and allowed to stand at room temperature until crystals formed within ten days. The crystals were isolated by filtration and dried in air. Yield: *Ca*. 69% based on Co. Elemental analysis: Anal. Calc. for $C_{40}H_{34}CoN_{14}O_4$: C 57.62, H 4.11, N 23.52 %. Found: C 57.76, H 4.14, N 24.36 %.

Synthesis of {[Co(4,4'-bpy)$_2$][(imdn)$_2$(H$_2$O)$_4$]}$_n$. (2):

Synthesis of **2** is the similar to that of **1**, but using 4,4'-bpy (30 mg, 0.19 mmol) instead of 2,2'-bpy. The crystals were isolated by filtration and dried in air. Yield: *Ca*. 78% based on Co. Anal. Calc. for $C_{30}H_{26}CoN_{12}O_4$: C 53.18, H 3.87, N 24.81 %. Found: C 53.01, H 3.57, N 25.01%.

(3) X-ray Crystallography

Single crystals of the complexes **1-2** with appropriate dimensions were chosen under an optical microscope and mounted on a glass fiber for data collection. X-ray crystallography: Single-crystal X-ray diffraction was performed using a Bruker Apex II CCD diffractometer equipped with a fine-focus sealed-tube X-ray source (Mo Kα radiation, graphite monochromated). Structures were solved by direct methods using SHELXTL and were refined by full matrix least squares on F^2 using SHELX-97. All the non-hydrogen atoms were treated anisotropically. Hydrogen atoms were placed in calculated positions with isotropic displacement parameters set to 1.2 U_{eq} of the attached atom.

(4) Table S1: Crystal data for 1 and 2

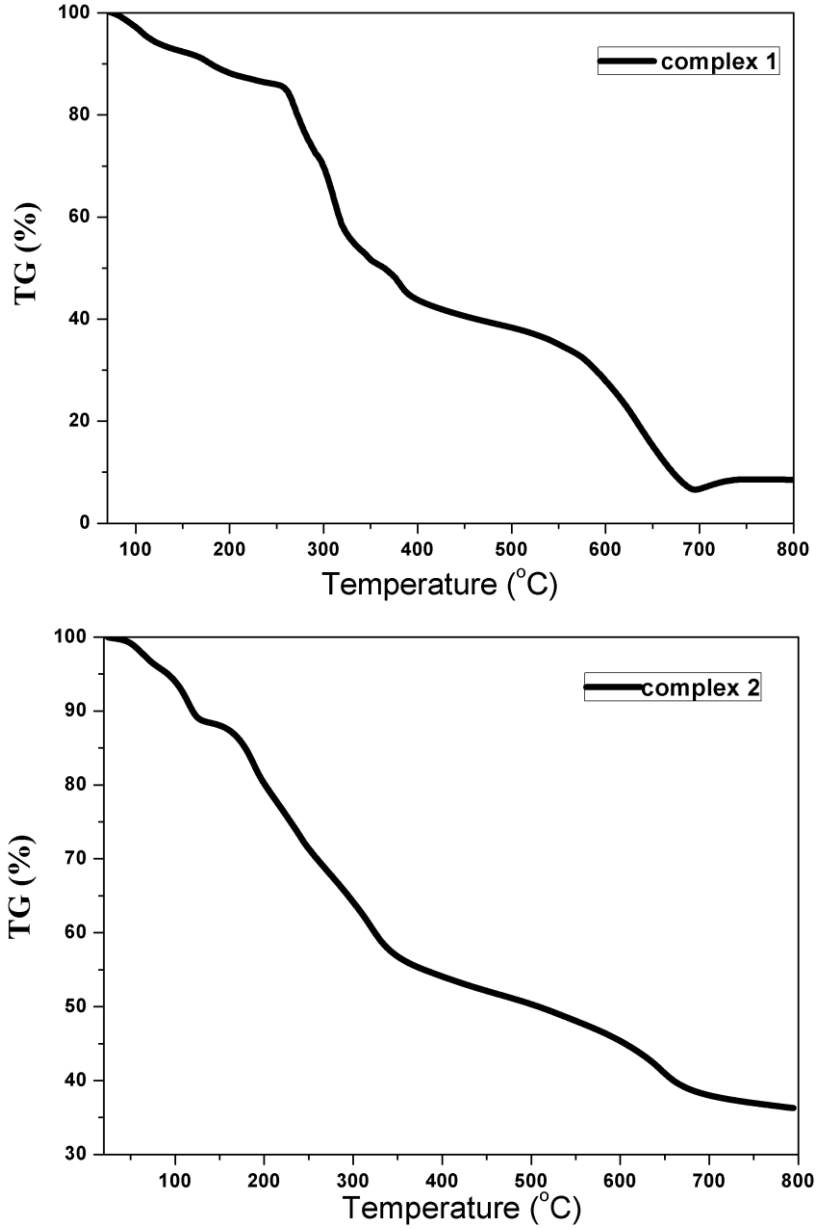
Compound	**1**	**2**
Empirical formula	$C_{40}H_{34}CoN_{14}O_4$	$C_{30}H_{26}CoN_{12}O_4$
Formula weight	833.74	677.56
Crystal system	Monoclinic	Tetragonal
Space group	$P2_1/c$	$I4_1cd$
a (Å)	9.8648(9)	16.2028(3)
b (Å)	29.440(2)	16.2028(3)
c (Å)	13.9210(13)	24.4818(9)
β (deg)	94.890(2)	90
V(Å^3)	4028.2(6)	6427.2(3)
T(K)	173(2)	173(2)
Z, D_{calcd} (Mg/m^3)	4, 1.375	8, 1.400
F(000)	1724	2792
μ(mm^{-1})	0.486	0.590
Ref. collected/unique	19965 / 7084	12005 / 3147
R_{int}	0.0484	0.0595
Parameters	532	214
Final R indices[$I > 2\sigma(I)$]	$R_1 = 0.0423$	$R_1 = 0.0372$
	$wR_2 = 0.0918$	$wR_2 = 0.0743$
R indices (all data)	$R_1 = 0.0681$	$R_1 = 0.0799$
	$wR_2 = 0.1040$	$wR_2 = 0.0891$
GOF	1.013	0.988
Completeness (%)	99.9	99.9
Max./ min., $\Delta\rho$ (e·Å^{-3})	0.275 / -0.288	0.246 / -0.357

$R_1 = \Sigma| |F_o|-|F_c| |/ \Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2-F_c^2)^2]/ \Sigma w(F_o^2)^2]^{1/2}$

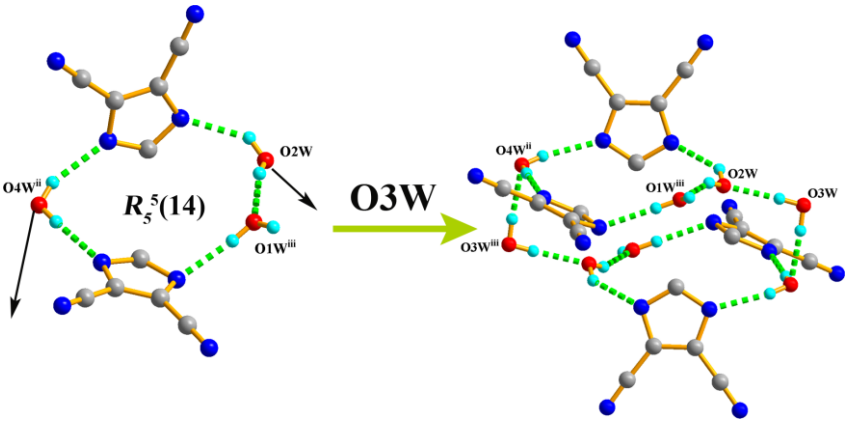
(5) Table S2: The selected bond distances and angles for 1 and 2

Compound **1**			
Co1—N2	2.109 (2)	Co1—N1	2.132 (2)
Co1—N6	2.1164 (19)	Co1—N4	2.140 (2)
Co1—N5	2.126 (2)	Co1—N3	2.154 (2)
N2—Co1—N6	98.92 (8)	N5—Co1—N4	97.05 (8)
N2—Co1—N5	93.04 (8)	N1—Co1—N4	95.31 (8)
N6—Co1—N5	77.05 (8)	N2—Co1—N3	93.90 (8)
N2—Co1—N1	76.94 (8)	N6—Co1—N3	97.38 (8)
N6—Co1—N1	171.48 (8)	N5—Co1—N3	171.71 (8)
N5—Co1—N1	95.61 (8)	N1—Co1—N3	90.37 (7)
N2—Co1—N4	167.86 (8)	N4—Co1—N3	76.63 (8)
N6—Co1—N4	89.93 (7)		
Compound **2**			
Co1—O2W	2.043 (6)	Co1—N2^{ii}	2.166 (2)
Co1—O1W	2.065 (5)	Co1—N1^{iii}	2.202 (2)
Co1—N2^{i}	2.166 (2)	Co1—N1	2.202 (2)
O2W—Co1—O1W	180.000 (1)	N2^{i}—Co1—N1^{iii}	89.40 (9)
O2W—Co1—N2^{i}	90.19 (13)	N2^{ii}—Co1—N1^{iii}	90.60 (9)
O1W—Co1—N2^{i}	89.81 (13)	O2W—Co1—N1	90.11 (13)
O2W—Co1—N2^{ii}	90.19 (13)	O1W—Co1—N1	89.89 (13)
O1W—Co1—N2^{ii}	89.81 (13)	N2^{i}—Co1—N1	90.60 (9)
N2^{i}—Co1—N2^{ii}	179.6 (3)	N2^{ii}—Co1—N1	89.40 (9)
O2W—Co1—N1^{iii}	90.11 (13)	N1^{iii}—Co1—N1	179.8 (3)
Symmetry codes: (i) $-x+1/2, y+1/2, z$; (ii) $x+1/2, -y-1/2, z$; (iii) $-x+1, -y, z$.			

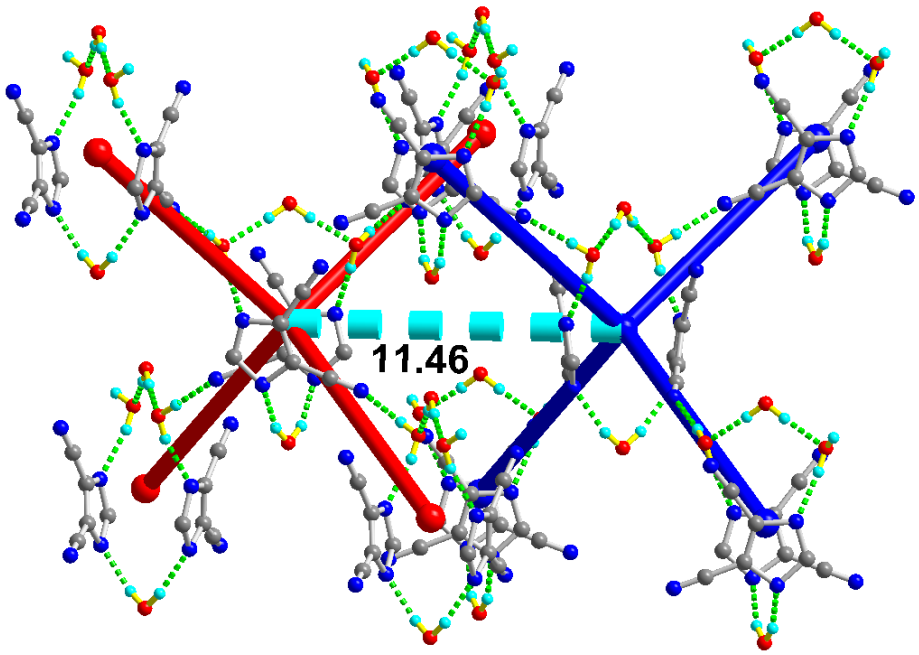
(6) Fig. S1: The TGA curve of 1 and 2



(7) Fig. S2: The $R_5^5(14)$ motif in the 1D imdn-water aggregation of 1



(8) Fig. S3: The adjacent independent tetrahedral nodes with a separation of 11.46 Å in 2



(9) Fig. S4: The relationship between the 2D coordination nets (green) and 3D supramolecular diamond nets (red and blue) in 2