Supporting Information

Quest for Extended Coordination Networks from High Connected Azido-Bridged Clusters

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Table S1. Selected bond lengths [°] and angles [Å] for **1** and **2**.

		1	
Co1—O3^{i}	2.070(5)	Co1—N1	2.164(5)
Co1—O1	2.077(5)	Co1—N1^{iii}	2.185(5)
Co1—O2^{ii}	2.126(4)	Co1—N1^{iv}	2.193(6)
Co1—N1—Co1^{vi}	141.7(3)	Co1—N1—Co1^{ii}	91.7(2)
Co1^{vi}—N1—Co1^{ii}	91.1(2)		
^{i} −*y*+1/3, *x*−*y*−1/3, *z*−1/3; ^{ii} *y*+1/3, −*x*+*y*+2/3, −*z*+2/3; ^{iii} −*y*+1, *x*−*y*, *z*; ^{iv} *x*−*y*+1/3, *x*−1/3, −*z*+2/3; ^{v} −*x*+*y*+2/3, −x+1/3, *z*+1/3; ^{vi} −*x*+*y*+1, −*x*+1, *z*.			
		2	
Co1—O2^{i}	2.064(6)	Co1—O3^{ii}	2.097(6)
Co1—O1	2.078(6)	Co1—N4^{iii}	2.100(7)
Co1—N4	2.080(7)	Co1—N1	2.422(6)
Co1—N4—Co1^{i}	100.8(3)	Co1—N1—Co1^{iii}	83.4(2)
Co1^{i}-N1-Co1^{iii}	140.2(7)		
^{i} *y*, −*x*+1/2, *z*; ^{ii} −*y*, x−1/2, −*z*+2; ^{iii} −*y*+1/2, *x*, *z*; ^{iv} *y*+1/2, −*x*, −*z*+2.			

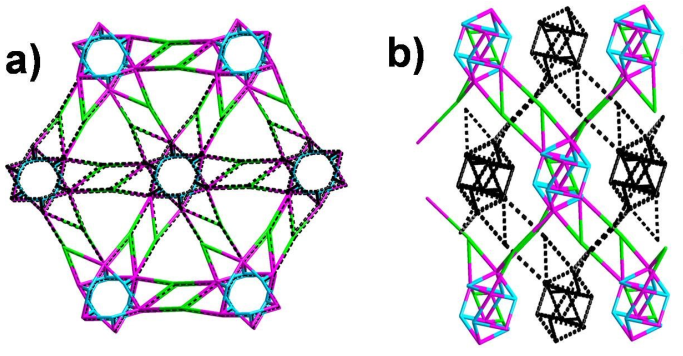


Fig. S1 a) Front view of the (3,6)-connected 3-nodal topological net of **1**. b) Side view of 3D network of **1**.

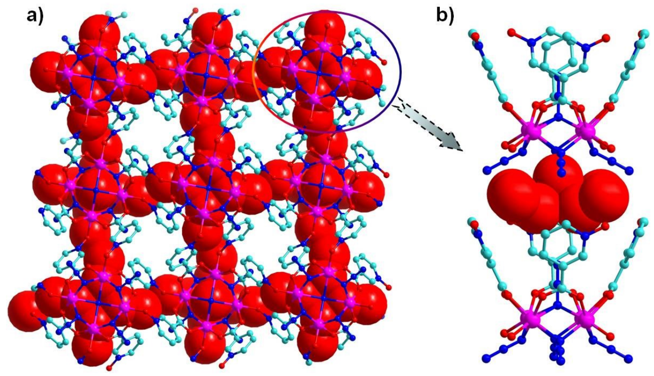
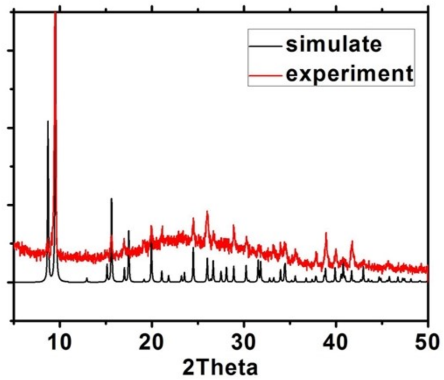
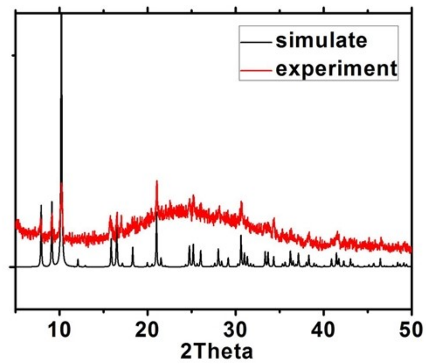


Fig. S2 a) The two-dimensional layers of **2** containing protonated water aggregate. b) The protonated water clusters $H^+(H_2O)_5$ are stabilized in two goblets of **2**.



a)



b)

Fig. S3 The XRPD diagrams for complexes: a) for **1**, b) for **2**.

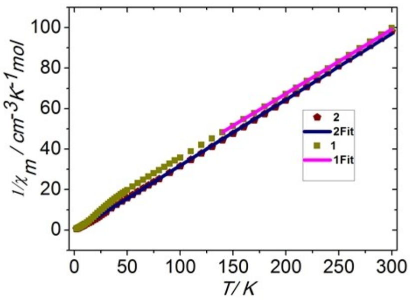


Fig. S4 Curie plots of **1** and **2** and the best-fit of the data through Curie–Weiss law.

Table S2. The Co-N-Co angle and magnetic coupling in some EO bridged cobalt complexes.

Co-N-Co angle (°)	*Bridges*	*Magnetic coupling*	*Ref*
93.60 and 93.68	Double EO azide and *syn,syn* carboxylate	F J = 10.7 cm^{-1}	1
97.2 and 97.6	Double EO azide and *syn,syn* carboxylate	F J = 13.9 cm^{-1}	2
94.74 and 96.83	Double EO azide and *syn,syn* carboxylate	F J =13.2cm^{-1}	3
95.85 and 95.85	Double EO azide and *syn,syn* carboxylate	F J = 8.1 cm^{-1}	3
94.54 and 94.76	Double EO azide and *syn,syn* carboxylate	F J = 13.8 cm^{-1}	3
95.47 and 97.4	Double EO azide and *syn,syn* carboxylate	F J = 10.6 cm^{-1}	4
94.73 and 96.24	Double EO azide and *syn,syn* carboxylate	F J = 8.1 cm^{-1}	5
95.49 and 94.99	Double EO azide and *syn,syn* carboxylate	F	6
96.29 and 92.23	Double EO azide and *syn,syn* carboxylate	F	7
92.79 and 93.38	Double EO azide and *syn,syn* carboxylate	F J = 13.96 cm^{-1}	8
91.62 and 91.67	Double EO azide and *syn,syn* carboxylate	F	9
129	EO azide, *syn,syn* carboxylate and O	F	10
120.74	Double *syn,syn* carboxylate and EO azide	F	11
114.51	Double *syn,syn* carboxylate and EO azide	F	12
122	Double *syn,syn* carboxylate and EO azide	F J = 54.1 cm^{-1}	13
115.12	Double *syn,syn* carboxylate and EO azide	F J = 10.3 cm^{-1}	14
116.14	Double *syn,syn* carboxylate and EO azide	F J = 66.8 cm^{-1}	15
124.37	*syn,syn* carboxylate and EO azide	F	16
128	*syn,syn* carboxylate and EO azide	F	17
117.3	*syn,syn* carboxylate and EO azide	F	18
120.09	*EO azide*	AF J = -2.98 cm^{-1}	18
112.3	EO azide	F	19
128.04	*syn,syn* carboxylate and EO azide	F	20
123.88	*syn,syn* carboxylate and EO azide	F J = 7.86 cm^{-1}	21
122.10	*syn,syn* carboxylate and EO azide	F J = 2.06 cm^{-1}	21
112.93	*syn,syn* carboxylate and EO azide	F	22
127.42	*syn,syn* carboxylate and EO azide	F J = 31.0 cm^{-1}	23

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