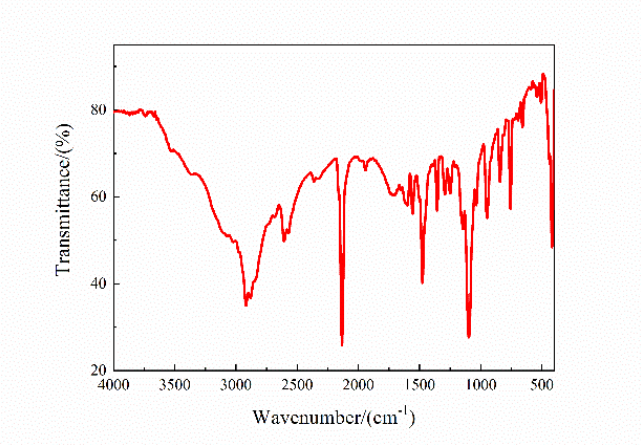

Figure S1. IR spectrum of compound **1.**

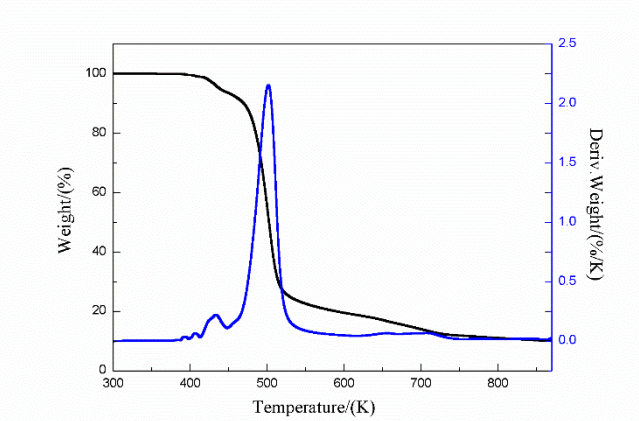

Figure S2. TG and DTA curves of compound **1.**

Table S2. Hydrogen bond N-H…O geometry (Å,°) for compound.

D-H…A	d(D…H)Å	d(H…A)Å	d(D…A)Å	D-H…A(°)
		100 K		
N_1-H_{1A} …O_1	0.910	2.554	2.832	98.290
N_1-H_{1B} …O_2	0.910	1.979	2.850	159.617
N_1-H_{1C} …O_3	0.911	3.015	3.188	92.573
N_1-H_{1A} …O_3	0.910	2.175	3.014	153.022
N_4-H_{4A}…O_4	0.887	1.828	2.704	168.82
O_4-H_{4C}…O_4	0.829	2.171	2.489	102.68
O_4-H_{4B}…N_2	0.869	1.888	2.744	167.59
N_1-H_{1C}…N_3	0.910	1.931	2.776	153.61
		296 K		
N_1-H_{1A} …O_1	0.890	2.595	3.220	128.008
N_1-H_{1B} …O_1	0.891	2.249	3.092	157.647
N_1-H_{1A} …O_2	0.890	1.997	2.844	158.524
N_1-H_{1B} …O_3	0.891	2.526	2.861	102.982
N_3-H_{3A}…O_4	0.826	1.935	2.732	161.66

O_4-H_{4A}…O_4	0,848	2.140	2,479	103.43
O_4-H_{4B}…N_2	0.850	1.902	2.715	159.78
N_1-H_{1C} …N_4	0.890	1.950	2.761	150.75

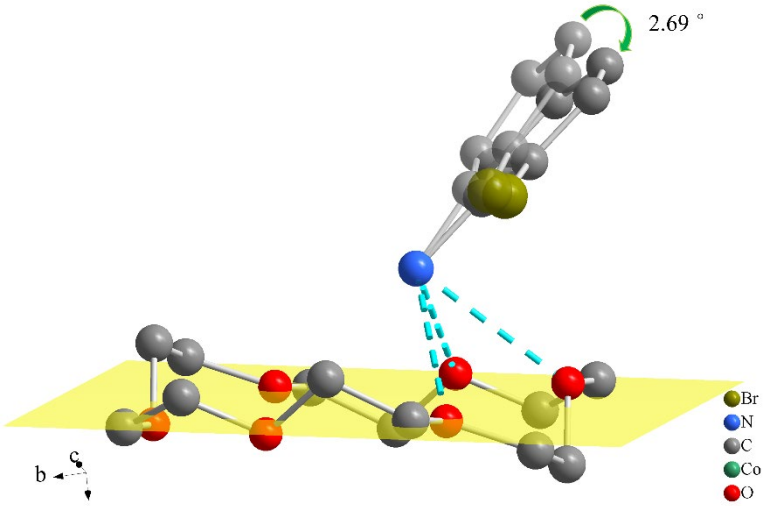

Figure S3. Swing diagram of crown ether cation complex o-BrAH of compound **1** at room and low temperature.

Through the information in Table 2, it can be concluded that the N-H···O type hydrogen bond is formed between the N atom in the $(o\text{-BrAH})^+$ ion and the oxygen atom in the 18-crown-6. The 18-crown-6 and the $(o\text{-BrAH})^+$ ion form two planes with an angle. The 18-crown-6 is considered as a planar body, and the $(o\text{-BrAH})^+$ ions are also formed into a plane. It was found that the dihedral angle formed by these two planes changed from 40.83 ° at room temperature to 38.14 ° at low temperature, with a change of 7.05 %, indicating that this change would also lead to a certain physical property change of compound **1**.

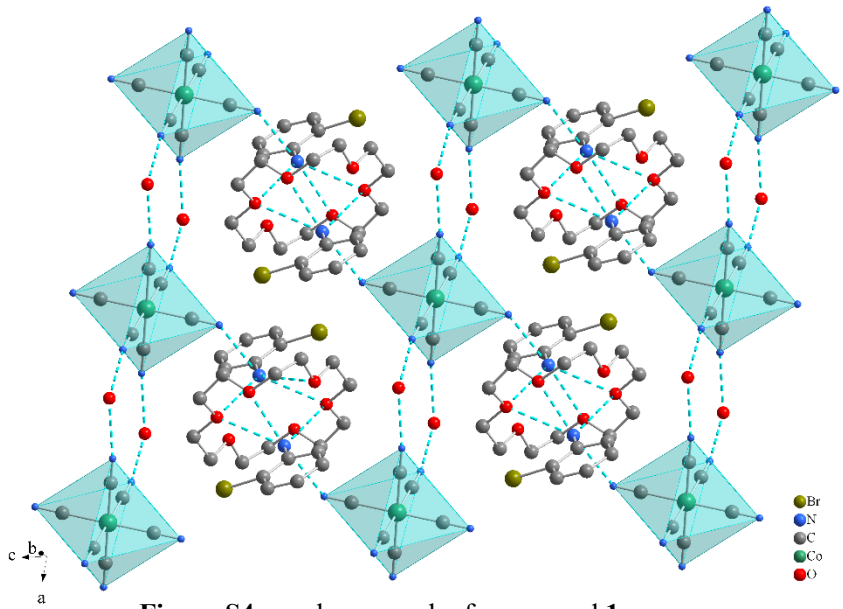

Figure S4. *ac* planar graph of compound **1.**

In the a-axis direction, $[H_2Co(CN)_6]$ is linked to two water molecules through the hydrogen bond of N-H···O to form a chain structure. In the c-axis direction, it is formed by forming a supramolecular group with 18-crown-6 and $(o\text{-}BrAH)^+$ ions through the hydrogen bond link of N-H···N, so that compound 1 forms a more stable two-dimensional planar structure in the ac plane.

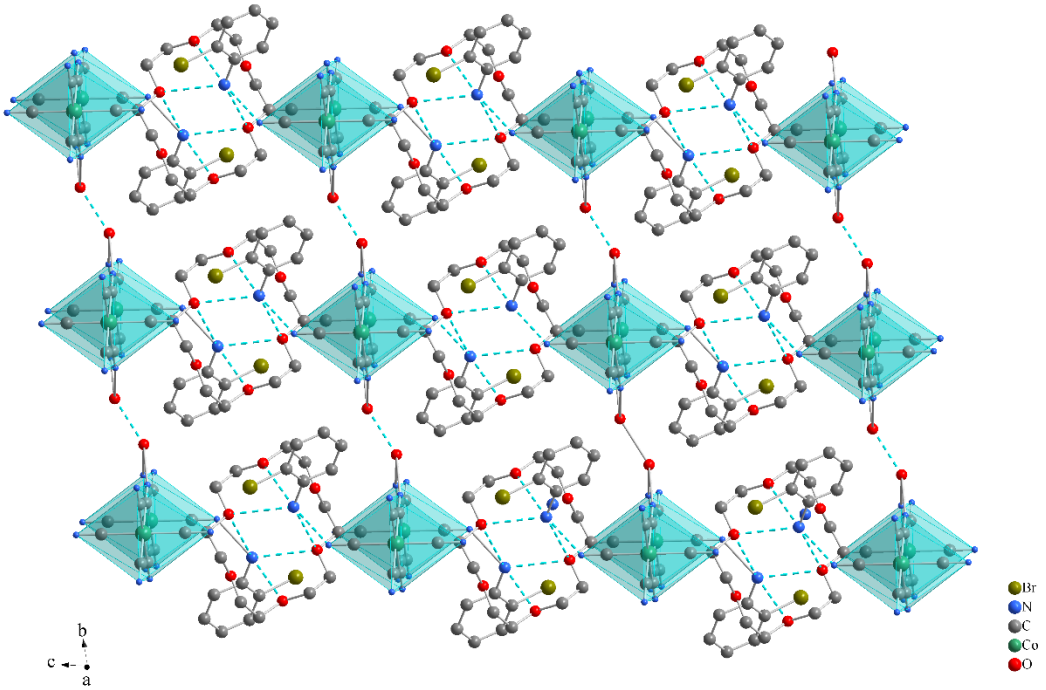

Figure S5. *bc* planar graph of compound **1.**

This is a two-dimensional structure diagram of compound **1** *bc* plane. Compound **1** forms a one-dimensional chain structure on the c-axis as shown in the above diagram, while the hydrogen bond type on the *b*-axis is N-H···O as the a-axis, but unlike the *a*-axis, it is connected by the lower $[H_2Co(CN)_6]$ and water molecules and then combined with the upper $[H_2Co(CN)_6]$ in the lower row to form a one-dimensional chain structure. It is proved that the compound forms a relatively stable three-dimensional network structure through intermolecular forces in the crystal cell.