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Structure Investigation of a Novel Nitrogen-rich Energetic Complex: Tetrammine-*cis*-bis(5-nitro-2*H*-tetrazole-N^2) Cobalt(Ⅲ) Perchlorate Dihydrate

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Energetic coordination compound with 5-nitro-tetrazole (NT) as ligand has gained more and more attentions due to its extreme explosive properties and ecological friendly pyrolysis products[1-6]. The research results in 1994 proposed from Sandia National Laboratories proves tetrammine-*cis*-bis (5-nitro-2*H*-tetrazole-N^2) cobalt (Ⅲ) perchlorate (BNCP) to be a more powerful explosive and undergoes deflagration-to-detonation (DDT) transition more rapidly than pentaammine (5-cyanotetrazolato-N^2) cobalt (Ⅲ) perchlorate (CP), has been used as a promising lead-free primary explosive in semiconductor bridge detonator, DDT detonator and laser ignition in the area of national defense in USA[2-3]. Superfine particles of BNCP was prepared and its properties was investigated by Yu and his co-workers, in 2007[7]. The crystal structures of BNCP determined at 293 K and 213 K were reported by Sandia National Laboratories in 1997 for the first time, which is agreement with each other closely[1]. Then, Sheng et al[8] obtained the same structure of BNCP, and reported more details. But now, we obtained a novel crystalline structure of tetrammine-*cis*-bis(5-nitro-2*H*-tetrazole-N^2) cobalt (Ⅲ) perchlorate dihydrate just with two lattice H_2O molecules, which exhibits a various packing method versus the anhydrous BNCP.

A Rigaku AFC-10/Saturn 724 + CCD diractometer with graphite monochromated Mo $K\alpha$ radiation (λ = 0.71073 Å) was applied for structure analyses. The structure was solved by direct methods using SHELXS-97[9] and refined by means of full-matrix least-squares procedures on F^2 with the SHELXL-97[10] program. Detailed information concerning crystallographic data collection and structure refinement is summarized in Table 1.

As shown in the Figure 1, the coordination environment of central Co atom of the title compound is similar to the anhydrous BNCP as reported[1,8]. Central Co atom coordinated with six N atoms from four ammonia molecules and two nitro-tetrazole anions, and formed an octahedral configuration. But, the hydrous BNCP is mirror symmetrically, the perchlorate ion is in the mirror plane along with the two crystal water molecules, rather than in the side of the molecule. Due to presence of two water molecules, a vast difference was induced on pack method of the unit cell between structure of hydrate and anhydrate BNCP. In the crystal structure of hydrous BNCP, a great number of hydrogen bonds intramolecularly and intermolecularly constructed by N and O atoms linked the molecules

Table 1 Crystallographic data and structure determination details for $[Co(CN_5O_2)_2(NH_3)_4]\cdot ClO_4\cdot 2H_2O$

crystal data	
$C_2H_{16}ClCoN_{14}O_{10}$	V = 864.8 (4) Å^3
M_r = 490.67	Z = 2
monoclinic, C_m	Mo $K\alpha$ radiation
a = 9.477 (3) Å	μ = 1.23 mm^{-1}
b = 12.362 (3) Å	T = 93 K
c = 8.316 (3) Å	0.40 mm × 0.30 mm × 0.20 mm
β = 117.429 (3)°	
data collection	
AFC10/Saturn 724 + diffractometer	1727 independent reflections
4359 measured reflections	1668 reflections with $I > 2\sigma(I)$
T_{max} = 0.791	R_{int} = 0.023
T_{min} = 0.639	θ_{max} = 27.5°
refinement	
$R[F^2 > 2\sigma(F^2)]$ = 0.023	$wR(F^2)$ = 0.051
1727 reflections	155 parameters
S = 1.00	6 restraints
$\Delta\rho_{max}$ = 0.38 eÅ^{-3}	$\Delta\rho_{min}$ = −0.32 eÅ^{-3}

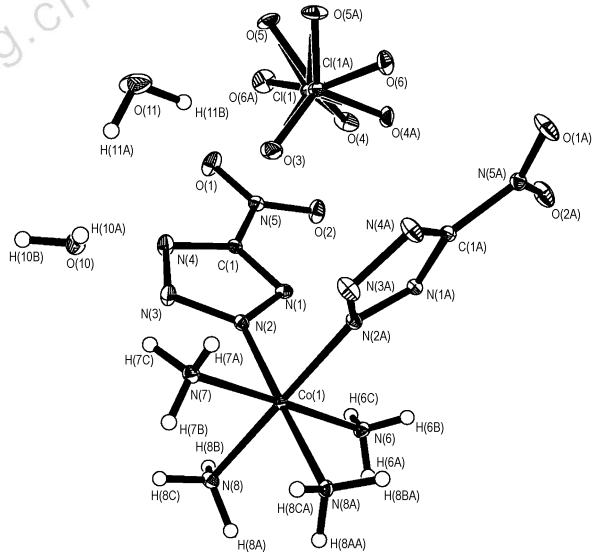

Fig. 1 Molecular structure of $[Co(CN_5O_2)_2(NH_3)_4]\cdot ClO_4\cdot 2H_2O$ showing the atoms-numbering scheme at 40% probability displacement ellipsoids, and the coordination environment of the central cobalt cation

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together and formed a three-dimensional neat structure. However, the hydrogen bonds of anhydrous BNCP just linked the molecules together to form a lamellar structure, and the layers were connected by the short contact. A hydrous BNCP molecule can form hydrogen bonds with eight other adjacent cobalt complexes through the nitrogen and oxygen atoms from nitro group, ammonia, water, perchlorate ion and the tetrazole ring. In the compound, there are two types of intramolecular hydrogen bonds constructed by O(10)—O(11) and O(11)—O(3). The two 4-site nitrogen atoms from the tetrazolyl rings contacted two N(8) atoms from the ammonia of two other hydrous BNCP molecules, which were joined by another cobalt complex through the hydrogen bonds formed between the two 4-site nitrogen atoms from tetrazolyl rings and N(8) from two ammonias. The four mentioned cobalt complexes constructed an rhombus with the length of 7.788 Å and an angle of 74.95 degree as showing in Figure 2. The rhombus reduplicated one by one to construct the net structure of the title compound. Futhermore, two O(2) atoms from nitro groups were joined together by the water molecule through O(10) from another hydrous BNCP molecule. Another crystal water molecule formed three intermolecular hydrogen bonds with three ammonias from the same another hydrous BNCP molecule. Due to presence of the crystal water, the hydrate is more insensitivity than anhydrate, in the process of thermolysis, and the crystal water was lost at a temperature of a bit more than 100 ℃.

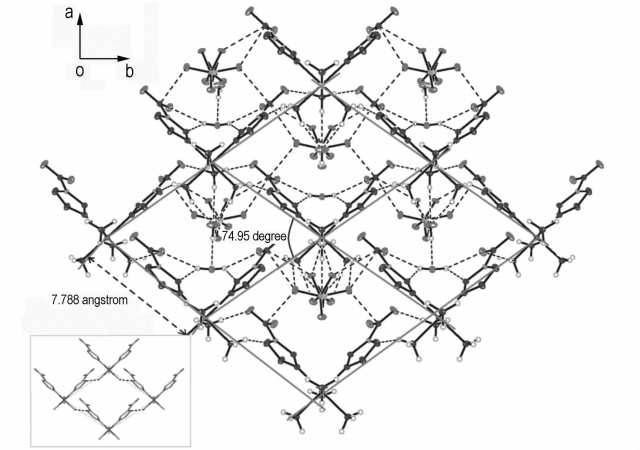

Fig. 2 Rhombus formed by four adjacent hydrous BNCP molecules, and the packing diagram of the title compound viewed along c axis

The crystal of a novel nitrogen-rich energetic coordination complex: tetrammine-*cis*-bis (5-nitro-2*H*-tetrazole-N^2) cobalt (Ⅲ) perchlorate dihydrate was obtained and characterized by using X-ray single-crystal diffraction. The crystal system of the compound is monoclinic with space groups C_m, and the coordination environment of central Co cation is similar to tetrammine-*cis*-bis (5-nitro-2*H*-tetrazoleN^2) cobalt (Ⅲ) perchlorate (BNCP), which does not include the two lattice H_2O molecules. However, due to the presence of the two water molecules, lots of different hydrogen bonds linked the molecules together and formed a three-dimensional neat structure.

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Key words: organic chemistry; nitrogen-rich energetic complex; tetrammine-*cis*-bis (5-nitro-2*H*-tetrazole-N^2) cobalt (Ⅲ) perchlorate (BNCP); crystal structure

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