Carbon-free energetic metal pentazolate hydrates

Subject Code: E04

With the support by the National Natural Science Foundation of China, a major breakthrough has been made by the group led by Prof. Lu Ming (**陆明**) from Nanjing University of Science & Technology. The related research achievement entitled "A series of energetic metal pentazolate hydrates" was published in *Nature* (2017, DOI: 10.1038/nature23662).

Singly or doubly bonded polynitrogen compounds can decompose to dinitrogen (N_2) with an extremely large energy release. This makes them attractive as potential explosives or propellants, but also challenging to produce in a stable form. In this work, Lu's group reported the synthesis and characterization of five metal (Na, Mn, Fe, Co, and Mg) pentazolate hydrate complexes. With single crystal structures analysis, they systematically revealed the coordination and hydrogen bond interaction between N_5^- ion and metal cations, and investigated their thermodynamic stability. The result provides strong scientific basic support for researching and developing assembly of N_5^- ion and all-nitrogen cations. This research is very meaningful for promoting the development of nitrogen chemistry and ultrahigh-energetic materials and improving the energy level of explosives.

With an oxidizing reaction to cut the C-N bond of arylpentazole, their group successfully obtained NaN_5 hydrate as a white powder. After recrystallization, the $[Na(H_2O)(N_5)]\cdot 2H_2O$ was collected and verified by high resolution mass spectrum and ^{15}N NMR. Via the ion exchange reaction between N_5 sodium salt and $MnCl_2$, $FeCl_2$, $Co(NO_3)_2$, $MgCl_2$, the corresponding crude products were gotten. Also after recrystallization, the $[Mn(H_2O)_4(N_5)_2]\cdot 4H_2O$, $[Fe(H_2O)_4(N_5)_2]\cdot 4H_2O$, $[Co(H_2O)_4(N_5)_2]\cdot 4H_2O$, and $[Mg(H_2O)_6(N_5)_2]\cdot 4H_2O$ were obtained and verified for their structures by single crystal structure X-ray diffraction. The synthetic process and single crystal structures are shown in Figure.

The series of energetic metal—N_5 complexes they have developed illustrates the adaptability of the *cyclo*-N_5^- unit in terms of its ability to take part in ionic, coordination and hydrogen-bonding interactions. Additionally, except cobalt-N_5 compound, the other four complexes all exhibit good thermostability (decomposition temperature>100℃). In view of their good stability and energy characteristics, Lu et al. anticipate that this feature will enable the development of other complexes, such as novel nitrogen-based analogues of metallocenes, complexes in which non-metallic elements stabilize the *cyclo*-N_5, or even polynitrogen energetic materials.

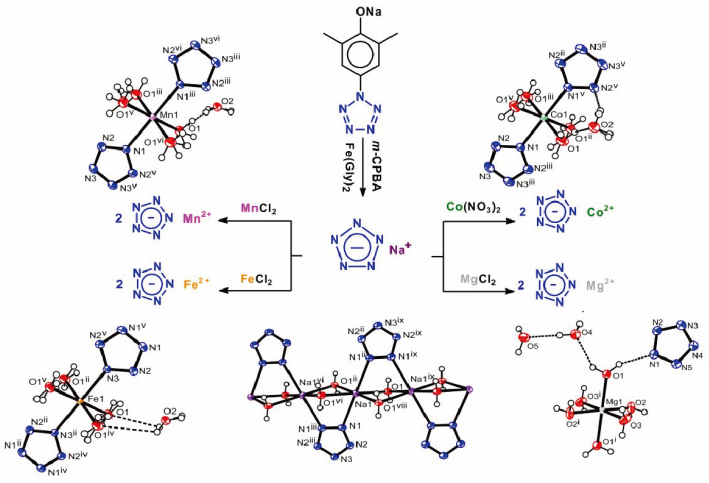

Figure Single-crystal X-ray analysis of prepared complexes.