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Preparation, crystal structures and thermal decomposition of three energetic manganese compounds and a salt based on imidazole and picrate

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ABSTRACT

The multi-ligand coordination compound of $[Mn(H_2O)_6](PA)_2{\cdot}2H_2O$ (**1**), $[Mn(IMI)_2(H_2O)_4](PA)_2$ (**2**) and $[Mn(IMI)_6](PA)_2{\cdot}H_2O$ (**3**), and a salt of $(IMI)(PA){\cdot}H_2O$ (**4**) were synthesized by using imidazole (IMI) and picrate (PA). Furthermore, they were characterized by elemental analysis and FT-IR spectrum. The crystal structures were determined by X-ray single crystal diffraction. The obtained results show the crystals of **1** and **4** belong to *orthorhombic*, *Pccn* and $Pna2_1$ space groups, and the crystals of **2** and **3** belong to *monoclinic*, $P2_1/c$ space groups. The metal Mn(II) cations are six-coordinated and exhibit distorted-octahedral configuration. Under nitrogen atmosphere with a heating rate of 10 K min^{-1}, the thermal decompositions contain two main exothermic stages in the DSC curves corresponding to TG–DTG curves. The non-isothermal kinetics parameters were calculated by the Kissinger's method and Ozawa's method, respectively. The energies of combustion, enthalpies of formation, critical temperatures of thermal explosion, entropies of activation ($\Delta S^{\neq}$), enthalpies of activation ($\Delta H^{\neq}$), and free energies of activation ($\Delta G^{\neq}$) were measured and calculated. In the end, the sensitivity properties were also determined with standard methods.

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1. Introduction

Long term use of mercury fulminate, lead azide and lead styphnate as primary explosives had resulted in serious environmental harms and health hazard problem for both military and civilian personnel. Fortunately, energetic coordination compounds represent an interesting class of high-energy-density materials (HEDMs) have aroused considerable attentions of the chemist. The synthesis and development of new energetic materials continues to focus on new heterocycles with high densities, high heats of formation, and good oxygen balance [1,2]. The chemists have done lots of studies about nitrogen-rich energetic compounds on the basis of imidazole [3–9], triazole [10–15] and tetrazole [16–22].

Imidazole (IMI) is pentacyclic heterocyclic compound containing three carbon atoms and two potential nitrogen coordination atoms. Imidazole derivative compounds, which are widely used in energetic materials, agriculture, medicine and other fields, can obtain through the following ways. Firstly, a new compound was synthesized by introducing azido or nitro explosive groups in IMI group, such as 2-azido-imidazole [8], nitro-imidazole [23], dinitro-imidazole [3,4,24–26], trinitro-imidazole [5,27], and so on. Secondly, the general methods for the preparation of energetic salts based on IMI are by neutralization or metathesis reactions with N-protonated cations such as ammonium, hydrazinium, etc., and C-, N-, or O-deprotonated anions such as picrate [8]. Furthermore, the role of the imidazole ring as metal binding site in compounds is well-known. In our previous study, $Cu(IMI)_4(N_3)_2$ [28], $Ni(IMI)_4(N_3)_2$ [28], $[Ni(IMI)_6](ClO_4)_2$ [7], $[Ni(IMI)_6](NO_3)_2$ [7] and $[Cu(IMI)_4](PA)_2$ [9] are the nitrogen-rich materials and their nitrogen contents are 46.70%, 47.27%, 25.23%, 33.17% and 24.74%. They had the extreme potential application as energetic materials in the near future.

In order to deepen the studies on the imidazole compounds, $[Mn(H_2O)_6](PA)_2{\cdot}2H_2O$ (**1**), $[Mn(IMI)_2(H_2O)_4](PA)_2$ (**2**) and $[Mn(IMI)_6](PA)_2{\cdot}H_2O$ (**3**) and $(IMI)(PA){\cdot}H_2O$ (**4**) were synthesized and their crystal structures and the thermal decomposition mechanisms were studied in the present work.

2. Experimental

General caution: The title compounds are energetic materials and tend to explode under certain conditions. Appropriate safety precautions (safety glasses, face shields, leather coat and ear plugs) should be taken, especially when the compound is prepared on a large scale and in dry state.

2.1. Materials and physical techniques

All the reagents and solvents were of analytical grade and used without further purification as commercially obtained.

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Elemental analyze was performed on a Flash EA 1112 full-automatic trace element analyzer. The FT-IR spectra was recorded on a Bruker Equinox 55 infrared spectrometer (KBr pellets) in the range of 4000–400 cm^{-1} with a resolution of 4 cm^{-1}. DSC and TG measurements were carried by using Pyris-1 differential scanning calorimeter and Pyris-1 thermogravimetric analyzer (Perkin Elmer, USA) under dry nitrogen as atmosphere with flowing rate of 20 ml min^{-1}. The combustion heat was menstruated by oxygen bomb calorimetry (Parr 6200, USA) in an oxygen atmosphere at a pressure of 3.10 MPa.

2.2. Synthesis idea

Experiments using Mn(II) and IMI in the molar ratios from 1:6 to 1:3 by conventional method 1, resulted in compound **2** and a large number of salt **4** as evidenced by IR spectroscopy and DSC analysis. Surprisingly, we can get our main synthetic product compound **3** by method 2. Therefore, we found metal Mn(II) cation was coordinated with six water by studying the crystal structure of Mn(II) and picric and the crystal structure was $[Mn(H_2O)_6](PA)_2 \cdot 2H_2O$ (**1**). This also explains why the picrate compounds have some coordinated waters [29] (Scheme 1).

2.3. Synthesis of *1*

The picric acid (about 38 mmol) was added to a solution of manganese carbonate (20 mmol) in 50 ml deioned water and was stirred for 5 min at 60 °C. Then the solution was cooled to room temperature. After filtration, the solution of title compound was obtained. The yield was 80% (based on Mn(II)). Elemental analysis for $MnC_{12}H_{20}N_6O_{22}$ (molar mass: 655.28 g mol^{-1}), calc.: C 22.00; H 3.38; N 12.83; found: C 21.89; H 3.43; N 12.87. IR (cm^{-1}, KBr pellets): 3393, 3082, 1633, 1561, 1334, 1271, 905, 705.

2.4. Synthesis of *2*

Compound **1** (10 mmol) was dissolved in distilled water (30 ml), and then charged into a glass reactor with a water bath. It was kept under mechanical stirring and heated to the temperature of 60–70 °C. Imidazole (20 mmol) was dissolved in distilled water (20 ml) and subsequently it was added to the **1** aqueous solution during 25–30 min with continuous stirring. In the end, the solution was cooled to room temperature naturally. The yield was 43% (based on Mn(II)). Elemental analysis for $MnC_{18}H_{20}N_{10}O_{18}$ (molar mass: 719.38 g mol^{-1}), calc.: C 30.05; H 2.80; N 19.47; found (%):C 30.18; H 2.68; N 19.58. IR (cm^{-1}, KBr pellets): 3329, 2954, 2858, 1836, 1624, 1560, 1431, 1324, 1270, 1158, 1064, 926, 884, 798, 745, 654, 609, 524.

2.5. Synthesis of *3*

$Mn(NO_3)_2 \cdot 4H_2O$ (10 mmol) was dissolved in distilled water (30 ml), and then charged into a glass reactor with a water bath. It was kept under mechanical stirring and heated to the temperature of 60–70 °C. Imidazole (60 mmol) and Li(PA) (picric lithium, 18 mmol) were dissolved in distilled water (20 ml) and subsequently they were added to the Mn(II) aqueous solution during 25–30 min with continuous stirring. In the end, the solution was cooled to room temperature naturally. The yield was 62% (based on Mn(II)). Elemental analysis for $MnC_{30}H_{32}N_{18}O_{16}$ (molar mass: 955.68 g mol^{-1}), calc.: C 37.71; H 3.38; N 26.38; found: C 37.62; H 3.47; N 26.22. IR (cm^{-1}, KBr pellets): 3321, 1616, 1569, 1554, 1534, 1489, 1432, 1364, 1321, 1275, 1256, 1161, 1093, 1072, 852, 742, 706, 660, 613, 517.

2.6. Synthesis of *4*

The picric acid (about 20 mmol) was added to a solution of IMI aqueous (20 mmol) in 30 ml deioned water and was stirred for 5 min at 60 °C. Then the solution was cooled to room temperature. After filtration, the solution of title compound was obtained. The yield was 82% (based on IMI). Elemental analysis for $C_9H_9N_5O_8$ (molar mass: 315.21 g mol^{-1}), calc.: C 34.30; H 2.88; N 22.22; found: C 34.26; H 2.89; N 22.18. IR (cm^{-1}, KBr pellets): 3327, 3162, 3087, 2997, 11632, 1564, 1491, 1431, 1366, 1276, 1160, 1083, 1051, 910, 790, 767, 745, 704, 621.

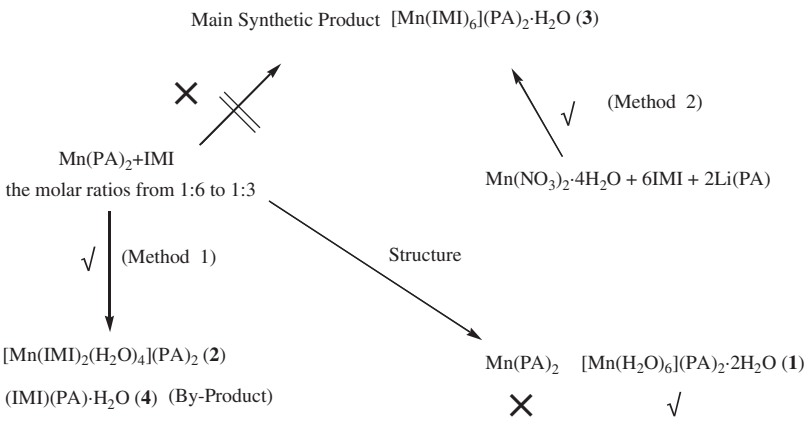
2.7. X-ray data collection and structures refinement

The X-ray diffraction data collection were performed on a Rigaku AFC-10/Saturn 724$^+$ CCD detector diffractometer with graphite monochromated Mo $K\alpha$ radiation (λ = 0.71073 Å). The structures were solved by direct methods using SHELXS-97 (Sheldrick, 1990) [30] and refined by full-matrix least-squares methods on F^2 with SHELXL-97 (Sheldrick, 1997) [31]. And all non-hydrogen atoms were obtained from the difference Fourier map and subjected to anisotropic refinement by full-matrix least squares on F^2. Detailed information concerning crystallographic data collection and structures refinement are summarized in Table 1.

3. Results and discussion

3.1. Crystal structures

In our previous study, the highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) of the IMI group are shown in Fig. 1 and the electronic density of



Scheme 1. Synthesis idea and synthesis line of the title compounds.

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