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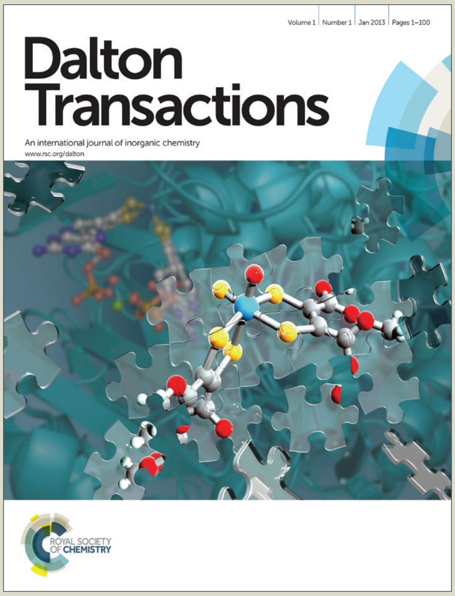

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Controllable explosion: Fine-tuning the sensitivity of high-energy complexes

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Tuning the sensitivity of energetic materials has always been a research topic of interest. A lot of attention has been paid on changing the ligands previously in traditional high energy density materials (HEDMs). Recently, we have stepped further along this path by thinking from another angle-changing the metal centre. Herein, we report 4 transition metal complexes with the ligands 1,5-diaminotetrazole, which have similar structures but drastically different sensitivities. These differences are apparently due to different metal centres.

High energy density materials (HEDM) based on nitrogen-rich complexes [1] have been used as energy-storage materials, propellants and explosives[2]. Current interest mainly lies in the development of HEDMs with increased energetic performance and decreased sensitivity[1f, 3,4]. Most previous research focused on tuning the ligands or anions to improve the sensitivity on the basis of these backbones, such as protonated ligands by strong acid (nitric acid or perchloric acid)[5,6], methylated in acetontrile[6] or other azo groups[1c, 7]. However, little attention has been paid to the relationship between the metal centre and the impact sensitivity. Recently, we have found that the sensitivity can be controlled by changing the metal centres of the metal 1,5-diaminotetrazole (DAT) perchlorate complexes.

1,5-diaminotetrazole (DAT) [4e, 5a, 8] and its derivatives have been described as a typical representation of highly energetic compounds. In the development of the lead-free primary explosives[4e, 9], adding the DAT ligand introduces a new way of designing energetic materials. We have reported two crystalline perchlorate salts of Co and Cd DAT complexes before[10], which are quite sensitive towards impact and friction stimuli [11]. The lack of crystal water in the structures makes them promising primary explosives. However, due to the environmental unfriendliness of the heavy metal elements, we moved to investigate the first-row transition metals, by synthesizing $[Mn(DAT)_6](ClO_4)_2$ and $[Zn(DAT)_6](ClO_4)_2$, which have lower toxicity than $[Cd(DAT)_6](ClO_4)_2$ but have higher sensitivity. It is noticeable that the four complexes have similar octahedron structures but exhibit very different sensitivities. Here we present the newly synthesized complexes, $[Mn(DAT)_6](ClO_4)_2$(**1**), $[Co(DAT)_6](ClO_4)_2$(**2**), $[Zn(DAT)_6](ClO_4)_2$(**3**) and $[Cd(DAT)_6](ClO_4)_2$(**4**). The synthesis method and the structures of these complexes are summarized in Figure 1.

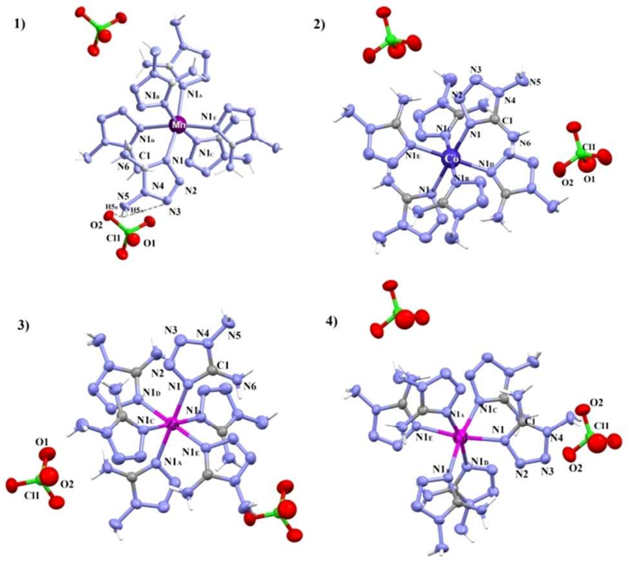

Figure 1. Structures of metal 1,5-diaminotetrazole perchlorate complexes ($[M(DAT)_6](ClO_4)_2$). 1) Crystal structure of $[Mn(DAT)_6](ClO_4)_2$where hydrogen atoms are shown in capped sticks style. Selected bond lengths [Å]: Mn-N1 2.290(10), N1-C1 1.336(15), N1-N2 1.379(14), N2-N3 1.284(15), N3-N4 1.365(14), N4-C1 1.343(15), N4-N5 1.389(14), N6-C1 1.332(16). 2) Crystal structure of $[Co(DAT)_6](ClO_4)_2$. Selected bond lengths [Å]: Co-N1 2.205(14), N1-C1 1.335(2), N1-N2 1.376(2), N2-N3 1.278(2), N3-N4 1.359(3), N4-C1 1.343(2), N4-N5 1.393(2), N6-C1 1.323(3). 3) Crystal structure of $[Zn(DAT)_6](ClO_4)_2$. Selected bond lengths [Å]: Zn-N1 2.218(11), N1-C1 1.332(2), N1-N2 1.373(2), N2-N3 1.274(2), N3-N4 1.355(3), N4-C1 1.339(2), N4-N5 1.386(2), N6-C1 1.317(3). 4) Crystal structure of $[Cd(DAT)_6](ClO_4)_2$. Selected bond lengths [Å]: Cd-N1 2.371(1), N1-C1 1.326(2), N1-N2 1.373(2), N2-N3 1.280(2), N3-N4 1.361(2), N4-C1 1.334(2), N4-N5 1.390(2), N6-C1 1.333(2).

The single-crystal X-ray diffraction study was performed for the crystals obtained through hydrothermal method. All the four crystals belong to the trigonal syngony. **1** and **4** crystallize in the space group $P\bar{3}c1$ while **2** and **3** crystallize in $P\bar{3}$. All the metal centres are hexa-coordinated through a strong electrostatic interaction with the nitrogen atom of of DAT. Hexa-coordinated energetic complexes are unusual and are only found in the structures of traditional CP/BNCP (2-(5-Cyanotetrazalato) pentaammine cobalt/tetraammine-*cis*-bis(5-nitro-2*H*-tetrazolato-*N*) cobalt) primary explosives.[12]

All the four complexes are shown in Figure 1. $[Mn(DAT)_6]^{2+}$ has a distorted octahedron geometry. All the six Mn-N bond lengths are the same (2.290(10) Å). The dihedral angle between different tetrazole planes is close to 31.7°, resulting from the

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steric effect from the bulky DAT groups.

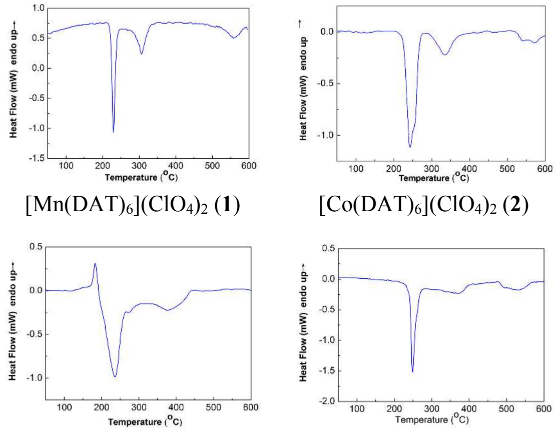
The cases are similar for the other three structures of $[Co(DAT)_6]^{2+}$, $[Zn(DAT)_6]^{2+}$ and $[Cd(DAT)_6]^{2+}$, which are distorted octahedrons as well (SI-Table S2). It should be noticed that hydrogen bonds play a quite important role in stabilizing the structures: the intermolecular hydrogen bonds form between amino groups and apical nitrogen atoms of DAT, while the intramolecular ones form between $-NH_2$ and ClO_4^-, which is similar to the structure of $[Mn(DAT)_6](ClO_4)_2$. The DAT ligands interact with each other through different types of hydrogen bonds (see the packing diagrams in Figure S1) , which leads to 2-D layered structures. (SI-Figure S2).

The decomposition of the four $[M(DAT)_6](ClO_4)_2$ samples was investigated using DSC and TG-DTG techniques (Figure 2 and SI-Figure S4).

The decomposition of **1** is a three-step process. The first and most rapid of decomposition occurs from 200.4 to 279.9 °C where the peak is at 242.8 °C. TG-DTG measurements show that about 65.6 wt% DAT decomposes in this period which is close to its theoretical capacity of 70.3 wt%. (The IR spectrum of **1**'s residue at 279.9 °C: $\nu_{N\text{-}H}$: 3324, 3256 cm^{-1}; $\nu_{C=N}$: 1322 cm^{-1}; $\delta_{N\text{-}H}$: 1600 cm^{-1} suggesting the cleavage of tetrazole ring.) New bands at 1620, 1514, 1423, 1097 and 628 cm^{-1} indicate the existence of [-CO-NH-] polymer and $Mn(ClO_4)_2$. At the same time, $Mn(ClO_4)_2$ ($\nu_{Cl\text{-}O}$: 1097 cm^{-1}) and $MnCO_3$($\nu_{C=O\&C\text{-}O}$: 1620, 1250 cm^{-1}) are detected. The continuous decomposition stage from 279.9 to 388.8 °C is possibly related to the formation (2117 cm^{-1}) of $Mn(NCO)_2$ and the decomposition of $Mn(ClO_4)_2$ with the mass loss of 21.4 wt%. Upon further heating to 600 °C, some black residue can be observed with some gas products. The black residue is identified as a mixture of MnO and MnO_2 based on IR data (SI-Figure S3, IR bands between 500 and 750 cm^{-1}).

There are three steps in the whole decomposition of **2** as well. The first stage is exothermic, from 213.8 to 250.9 °C, with the peak at 229.9 °C. The weight loss is 58.8 wt% corresponds to the ring opening activity. The next two stages are exothermic at a temperature range from 250.9 to 347.2 °C and 502 to 600 °C where the corresponding mass loss is 26.8 wt% and. 8.57 wt%, respectively. The final products (9.31 wt%) is Co_3O_4 based on IR spectra of the residue.

For **3**, a melting process starts at 170.5 °C. **3** starts to decompose at 185.6 °C and stops at 305.9 °C with the peak at 235.6 °C (56.0 wt% mass loss in total). This corresponds to a process of DAT ring opening and the formation of $Zn(ClO_4)_2$. The next two steps are both exothermic at the temperature range of 305.9-442.3 °C and 442.3-600 °C with the weight loss of 6.4 wt% and 10.8 wt%, respectively. The final residue (9.6 wt%) is ZnO.



$[Mn(DAT)_6](ClO_4)_2$ (**1**) $[Co(DAT)_6](ClO_4)_2$ (**2**)

$[Zn(DAT)_6](ClO_4)_2$ (**3**) $[Cd(DAT)_6](ClO_4)_2$ (**4**)

Figure 2. DSC traces of $[M(DAT)_6](ClO_4)_2$ (measured at 5°C/min to 600°C in nitrogen gas flowing with the rate of 20mL/min).

The decomposition of **4** is similar to the other three. The three stages occur at the temperature ranges of 230.0-281.8 °C (weight loss: 71.7 wt%), 301.7-476.9 °C (weight loss: 20.21 wt%) and 476.9-600 °C (weight loss: 20.21 wt%), respectively. The overall peak is at 249.3 °C. The final residue is CdO. Therefore, the decomposition processes of the four complexes should be described as follows (The IR spectrum of the corresponding products have been listed in the SI-Figure S3):

$$\begin{aligned} [M(DAT)_6](ClO_4)_2 &\longrightarrow M(ClO_4)_2 + M(CO_3) + [\text{-CO-NH-}]\ \text{polymer} + \text{gas} \\ &\longrightarrow M(NCO)_2 + \text{gas} \\ &\longrightarrow MO + \text{gas} \end{aligned}$$

We further applied Kissinger's and Ozawa-Doyle's method[13] (shown in equation (1) and (2)) to explore the activation energy of the first stage of the decomposition. In the equations, T_p means the peak temperature, R equals to 8.314 J/(mol·K), β is the linear heating rate set as 2, 5, 10 and 20 K/min. C represents a constant. A (s^{-1}) and E (kJ/mol) refer to pre-exponential factor and activation energy, respectively. The results have been listed in SI-Table S2. By averaging the results of K-method and O-method, the values of activation energy of the four complexes are 32.6, 37.2, 29.5 and 47.8 kcal/mol.

$$\ln\frac{\beta}{T_p^2}=\frac{RA}{E}-\left(\frac{E}{R}\right)\left(\frac{1}{T_p}\right) \quad (1) \qquad \ln\beta+\frac{0.4567\,E}{RT_p}=C \quad (2)$$

The sensitivity is analyzed by the sensitivity test (Table 1). Impact and friction sensitivity measurements were performed according to the standard BAM method.[14a] The measurement of flame sensitivity[14b] has been described in the supplementary information. Wherein **2** is sensitive to all the impact, friction and flame, **4** is sensitive to both the impact and friction while **3** is the most insensitive among the four complexes. The impact sensitivity suggests **2** and **4** are very sensitive (< 3J), while **1** is

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sensitive (<4 J, >3 J)[5a]. For **3**, it is highly stable because it is insensitive to the stimulation of all three factors. The friction sensitivities show the same trend as the impact sensitivities, while **2** is extremely sensitive to friction and should be handled carefully.

Table 1. The sensitivity of the four complexes

Complexes	Impact(J)	Friction (N)[a]	Flame (cm)
1	3.6	252	18.63
2	0.6	9 (+)	21.75
3	-	> 360	-
4	1.2	20 (+)	33.93

[a]: According to the *UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria*[14a], (+) indicates not safe for transport

Further insights into the electronic structures and HOFs (Heat of Formation) come from the studies with DFT. All structures were computed using the Gaussian 09[15a] with the method of unrestricted B3LYP[15b,c]. For the non-metal elements we used the Gaussian basis set[16] of 6-31+G*. For the metal elements, pseudo potential basis sets of LanL2DZ with f polarization corrections[17] have been used (2.195 for Mn, 2.780 for Co, 3.031 for Zn and 1.495 for Cd). The optimized structures are shown in SI-Figure S4. High spin and low spin states have been compared for the metal centres in **1** and **2** to confirm the electronic configurations. For Mn^{2+}, the electronic configuration is $(t_{2g})^3(e_g)^2$ which is 39.4 kcal/mol lower than the low-spin state of $(t_{2g})^5$. While forCo^{2+} it is $(t_{2g})^5(e_g)^2$ which is 16.1 kcal/mol lower than that of $(t_{2g})^6(e_g)^1$. Therefore, these two metal centres are both at high-spin states here. NBO analysis of the interactions between the DAT units and the transition metal centre at the ground states confirms that the dominant interactions are donation of electron density (i) from N1-C1 π orbital localized on N1 to the σ^* orbital of Mn-N1/Co-N1 or *non-bonding* (*n*) orbital of Zn/Cd localized on the metal and (ii) from metal σ/*n* orbital to N1-C1π^* orbital localized on N1. (Figure 3). The second order stabilization energy (*E*2) shows that the strength of the interactions of (i) and (ii) increases in the order of **2**<**4**<**1**<**3**, which results in the different stabilities of the compounds (SI-Table S3). This order of stability is consistent with the observed impact and friction sensitivities of the complexes together with our previous study of many energetic complexes[18] (SI-Table S4), we see that the sensitivities vary with different transition metal centres. Simply put, we believe that the metal with the electronic configuration of $3d^6$-$3d^9$ makes the complex more sensitive. To further confirm this conclusion, we also explored the *E2* of $[Fe(DAT)_6](ClO_4)_2$ and $[Ni(DAT)_6](ClO_4)_2$. The order of *E2* is $[Fe(DAT)_6](ClO_4)_2$<**2**< $[Ni(DAT)_6](ClO_4)_2$<**4**<**1**<**3**.

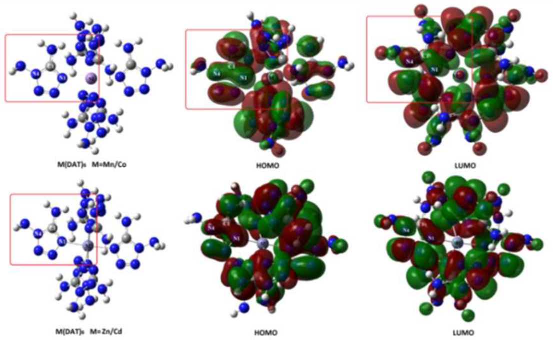

Figure 3.NLMOs of $[M(DAT)_6]^{2+}$ are boxed at the best view.

Table 2. Physical properties of the four complexes

Complexes	$\Delta_f H^\ominus$ [a]	$\Delta rH^\ominus$ [b]	Band gap[c]	Density[d]	E_k[e]	Impact sensitivity	Ti(°C) [f]
1	915.33	0.202	43.4	1.786	32.6	3.6	200.4
2	931.46	0.196	28.3	1.777	37.2	0.6	213.8
3	946.46	0.203	86.0	1.801	29.5	-	185.6
4	958.13	0.172	84.8	1.855	47.8	1.2	230.0

[a] Heat of formation (kcal/mol, Gaussian09 results); [b] Reactive enthalpy (kcal/mol, Gaussian09 results); [c] Band gap (kcal/mol, CASTEP results) [d] experimental densities (g/cm^3); [e] The activation energy of the first exothermic stage by Kissinger's method (kcal/mol) [f] Thermal decomposition temperature under nitrogen gas (DSC, 5 °C/min)

Ochterski's methods[19] were used to calculate the HOFs ($\Delta_f H^\ominus$). The reaction enthalpies ($\Delta_r H^\ominus$) of **1-4** are listed in Table 2. The 0 K HOF of metals are used as follows: 67.02 kcal/mol for Mn [20], 101.60 kcal/mol for Co[21], 31.04 kcal/mol for Zn [20] and 28.20 kcal/mol for Cd [21]. All the complexes have positive HOFs. Furthermore, the positive theoretical enthalpy of reaction implies that all the reactions are endothermic. The crystal structures and electronic structures of **1-4** were investigated using the MS CASTEP [22] package with the GGA-PBE functional. The optimized crystal structures are very similar to the previously reported crystallographic data for **1-4**. (SI-Figure S5). The band gaps of **1** to **4** are 43.4, 28.3, 86.0 and 84.8 kcal/mol, respectively. The DOS and *p*DOS are shown in SI-Figure S6. For **1** and **2**, the top of the valence band consists of Mn/Co 3*d* states, while for **3** and **4**, it consists of N/O 2*p* states. Combined with our results (Table 2 and SI-Table S5) [18], it is reasonable to conclude that the impact sensitivities are inversely proportional to the band gaps of the complexes $[M(DAT)_6](ClO_4)_2$, (M= Mn, Fe, Co, Ni, Cu, Zn). The density of most of the new perchlorate DAT complexes ranges between 1.77 and 1.85 g/cm^3. The decomposition temperatures lie in the range of 185-242 °C.

Conclusions

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We have reported four transition metal 1,5-diaminotetrazole complexes with similar structures but different explosive properties. DFT calculations confirm that the first row transition metal elements with electronic configuration of $3d^6$-$3d^9$ make the explosive more sensitive than those with the electronic configuration of $3d^5$ or $3d^{10}$. Last but not least, across the period, the impact sensitivities of this series of transition metal DAT complexes are inversely proportional to their band gaps.

Notes and references

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† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI:10.1039/b000000x/

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Graphical Abstract

The sensitivities are controllable just by tuning the centre metal centres in the energetic complexes of $[M(DAT)_6](ClO_4)_2$.