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Syntheses, crystal structures and thermal analyses of two new ionic complexes based on 3,4-diamino-1,2,4-triazole

JIN-TING WU, JIAN-GUO ZHANG*, XIN JIN, XIN YIN and TONG-LAI ZHANG

State Key Laboratory of Explosion Science and Technology, Beijing Institute of Technology, Beijing, China

Two new ionic complexes, (DATr)₂[Li₂(TNR)₂·2H₂O]·2H₂O (**1**) and (DATr)[Zn(DATr)Cl₃] (**2**), were synthesized by using 3,4-diamino-1,2,4-triazole (DATr) as outer cation. X-ray single-crystal diffraction analysis revealed that the two complexes crystallize in triclinic and orthorhombic crystal systems, respectively. Differential scanning calorimetry (DSC) was applied to assess the thermal decomposition behavior and kinetic parameters of decomposition were studied by using Kissinger's and Ozawa-Doyle's methods. Furthermore, the critical temperature of thermal explosion and parameters of thermodynamics were obtained.

Keywords: Complexes; 3,4-Diamino-1,2,4-triazole; Crystal structure; Thermal analysis

1. Introduction

Many efforts were made to explore new energetic materials aimed at meeting requirements of future military and civilian applications [1-3]. Nitrogen-rich compounds have attracted interest of materials chemists due to their potential applications, such as gas storage [4, 5], energetic metal-organic frameworks (MOFs) [3, 6, 7] and explosives [8-10]. Nitrogen-rich azoles have been widely studied and exhibit smokeless combustion, good thermal stability and positive heats of formation [11-15]. Their high heats of formation depend on the existence of a large number of

^{*}Corresponding author. Email: zjgbit@bit.edu.cn

N–N and C–N bonds [16-19]. Owing to nitrogen-rich azoles' merits, they are mainly used in the field of energetic materials [20-24].

As a high nitrogen azole [N% = 70.7], 3,4-diamino-1,2,4-triazole (DATr) is a promising energetic material. The two amino groups reduce the sensitivity and increase the possibility of hydrogen bonds that will enhance the thermal stability [25-27]. Thus, numerous ionic salts and complexes based on DATr have been reported [28-30]. Mostly DATr as neutral ligand was found in these reported coordination compounds. Research on complexes with central metal cation and DATr⁺ cation is rarely investigated, and the properties of complexes constructed by this unique combination are not well known.

Herein, complexes of nitrogen-rich cation 3,4-diamino-1,2,4-triazolium as the outer cation were synthesized and characterized. Their crystal structures were obtained and their thermal stabilities were also investigated.

2. Experimental

2.1. Materials and general methods

All reagents and solvents were of analytical grade and used without purification as commercially obtained. 3,4-Diamino-1,2,4-triazole was prepared according to the literature [31].

Elemental analyses were performed with a Flash EA 1112 full-automatic trace elemental analyzer. Infrared spectra were recorded by Fourier transform techniques on a Bruker Equinox 55 spectrometer (KBr pellets) from 4000 to 400 cm⁻¹. Differential scanning calorimetry (DSC) was carried out on a Pyris-1 differential scanning calorimeter.

2.2. Synthesis of 3,4-diamino-1,2,4-triazole (DATr)

Sodium hydrogen carbonate (0.84 g, 10 mmol) was slowly added to a solution of DATr·HCl (1.36 g, 10 mmol) in 10 mL of distilled water. The mixture was stirred until there was no further gas released and then the water was evaporated under vacuum, the mixture was dissolved in 30 mL absolute methanol and the inorganic salt was removed by filtration. After filtering, the

solvent was removed under reduced pressure to produce a colorless solid at 82% yield. IR (KBr, cm^{-1}): 3483, 3055, 1631, 1568, 1341, 1137, 962, 641. MS(DEI+): m/z=100.00[C₂H₆N₅⁺]. C₂H₅N₅ (99.11): calcd. C 24.24, H 5.09, N 70.67; found C 24.27, H 5.07, N 70.65.

2.3. Synthesis of $(DATr)_2[Li_2(TNR)_2 \cdot 2H_2O] \cdot 2H_2O(1)$

A mixture of DATr•HCl (0.41 g, 3 mmol) and LiOH (0.13 g, 3 mmol) in 15 mL of water was stirred at 45 °C while a solution of 2,4,6-trinitro-resresorcinol (styphnate acid) (0.74 g, 3 mmol) in methanol (20 mL) was added. After 30 min the precipitate was filtered and air-dried to yield **2** as a yellow solid. The yield was 34.3%. IR (KBr, cm⁻¹): 3427, 3336, 1658, 1615, 1350, 1214, 1027, 890. $C_{16}H_{22}Li_2N_{16}O_{20}$ (772.38): calcd. C 24.88, H 2.87, N 29.02; found C 24.81, H 2.90, N 29.05.

2.4. Synthesis of (DATr)[Zn(DATr)Cl₃] (2)

A solution of $ZnCl_2$ (50 wt%, 0.82 g) in 10 mL absolute methanol was added dropwise to solution of DATr (0.6 g, 6 mmol) in 20 mL absolute methanol under stirring at 40 ~ 45 °C. After 1 h, the precipitate was collected by filtration, rinsed with distilled water, and dried in air to yield 1 as a colorless solid. The yield was 37.4%. IR (KBr, cm⁻¹): 3412, 1691, 1472, 1330, 1232, 1016, 948. C₄H₁₁N₁₀Cl₃Zn (370.97): calcd. C 12.95, H 2.99, N 37.76; found C 12.99, H 2.92, N 37.77.



Scheme 1. Synthesis of **1** and **2**.

2.5. Crystal structure

The X-ray crystallographic data of **1** and **2** were obtained by using a Rigaku Saturn724+ CCD diffractometer equipped with graphite monochromated Mo K_{α} radiation. The structures were solved with successive Fourier difference syntheses (SHELXS-97) [32] and refined by full-matrix least-squares on F^2 using SHELXL-97 [33]. For all the structures, hydrogens were refined with riding model position parameters and fixed isotropically. Crystallographic data are summarized in table 1.

The two compounds crystallize in triclinic P-1 and orthorhombic Pna2(1) crystal systems, respectively. The detailed crystallographic data are listed in table 1 and their molecular structures are shown in figure 1 and figure 3.

The $[Li_2(TNR)_2 \cdot 2H_2O]^{2-}$ anion unit is made of two Li⁺ cations, two TNR²⁻ anions and two coordinated waters, in which the TNR²⁻ anions are chelating ligands linking the Li⁺ cations through eight oxygens. The Li⁺ is in a five-coordinate configuration by four oxygens of two TNR ligands and one O of crystal to form a trigonal bipyramid with Li–O bond lengths from 1.911 to 2.050 Å. In **1**, TNR is a chelating and bridging ligand. Two five-membered planar chelate rings were formed by Li1 and two TNRs, resulting in minimum steric hindrance. Plane equations are: A, 6.856x - 2.349y - 2.624z = 1.1681 for [Li1, O1, C1, C2, N6, O2] and B, 6.374x – 4.100y + 4.303z = -0.6751 for [Li1, O1A, O8A, C1A, C6A, N8A]. The angle between planes A and B is 165.5°.

Figure 3 reveals a Zn²⁺, one DATr, three chlorides and one DATr cation in (DATr)[Zn(DATr)Cl₃] (2). The Zn²⁺ is tetrahedral by three Cl⁻ [Zn–Cl distances from 2.2508(8) to 2.2736(8) Å] and one nitrogen of DATr ligand [Zn–N distance 1.993(2) Å].

The packing of the two compounds are shown in figures 2 and 4. Packing is strongly influenced by an intense hydrogen bond network within discrete layers but also between them. Furthermore, it can be seen from the packing diagram that intermolecular hydrogen bonds extend the structure into a 3D supramolecular structure, enhancing the thermal stability.

3. Results and discussion

3.1. Thermal stability and non-isothermal kinetic analysis

Differential scanning calorimetry (DSC) measurements to determine the decomposition temperatures of **1** and **2** were performed at a heating rate of 10 °C min⁻¹ (figure 5). For **1**, the DSC curve has a sharp endothermic process with peak temperatures of 190.4 °C, followed immediately by two exothermic stages with the corresponding peak temperature of 230.5 °C and 315.3 °C, respectively. The DSC curve of **2** showed that a main endothermic process at 187.3 -215.7 °C, then dramatic exothermic process from 266.7 - 329.0 °C as the top temperature was 306.3 °C. The thermal stability of **1** is lower than that of **2**, attributed to relatively lower stability of the nitro-rich TNR in **1** than that of chlorides in **2**, which is in agreement with the crystal structures.

The apparent activation energy (E) and the pre-exponential factor (A) were obtained by using Kissinger's method [34] and Ozawa-Doyle's method [35]. Based on the first exothermic peak temperatures measured with four different heating rates of 5, 10, 15, 20 °C •min⁻¹, Kissinger's and Ozawa-Doyle's methods were applied to study the kinetics parameters. The equations of Kissinger (1) and Ozawa-Doyle (2) are as follows:

$$\frac{d\ln\left(\beta/T_{p}^{2}\right)}{d(1/T_{p})} = -\frac{E_{a}}{R} \quad (1)$$
$$\log\beta + \frac{0.4567E_{a}}{RT_{p}} = C \quad (2)$$

where T_p (K) is the peak temperature; *R* is equal to 8.314 kJ·mol⁻¹·K⁻¹; β (K·min⁻¹) is the linear heating rate; *C* is a constant.

From the original data, the apparent activation energy E_k and E_o , linear coefficient R_k and R_o and pre-exponential factor A_k were obtained and summarized in table 2.

The calculated results from different methods correspond well with each other, and values are all in the normal range of kinetic parameters for thermal decomposition of solid materials. The apparent activation energy of $\mathbf{1}$ is 52.5 kJ·mol⁻¹ lower than $\mathbf{2}$, indicating the energy barrier for decomposition of $\mathbf{1}$ is smaller, in accord with the DSC curve.

The Arrhenius equation for the first exothermic process can be expressed by using *Ea* (the average of E_K and E_O) and $\ln A_K$ as follows:

ln $k = 9.135 - 109.8 \times 10^{3} / (RT)$ (for **1**) ln $k = 12.65 - 16.0 \times 10^{3} / (RT)$ (for **2**)

These two equations can be used to estimate the rate constants of the initial thermal decomposition process of $(DATr)_2[Li_2(TNR)_2\cdot 2H_2O]\cdot 2H_2O$ and $(DATr)[Zn(DATr)Cl_3]$.

3.2. Critical temperature of thermal explosion

The value of the peak temperature (T_{p0}) corresponding to $\beta \rightarrow 0$ was obtained by using equation 3, where *a*, *b* and *c* are coefficients.

$$T_{pi} = T_{p0} + a\beta + b\beta^2 + c\beta^3 \quad (3)$$

The corresponding critical temperatures of thermal explosion (T_b) is calculated by equation 4, where *R* is 8.314 kJ·mol⁻¹·K⁻¹; *E* is the value of E_k from Kissinger's method.

$$T_b = \frac{E - \sqrt{E^2 - 4ERT_{p0}}}{2R}$$
(4)

According to equations 5-7, the entropy of activation (ΔS^{\neq}) , enthalpy of activation (ΔH^{\neq}) and free energy of activation (ΔG^{\neq}) of the decomposition reaction corresponding to $T=T_{p0}$, $E_a=E_K$ and $A=A_K$ (obtained from Kissinger's method) were obtained [36],

$$A = \frac{k_B T}{h} e^{\Delta S^{\pm}/R} \quad (5)$$
$$\Delta H^{\pm} = E - RT \quad (6)$$
$$\Delta G^{\pm} = \Delta H^{\pm} - T\Delta S^{\pm} \quad (7)$$

where k_B is the Boltzmann constant $(1.381 \times 10^{-23} \text{ J} \cdot \text{K}^{-1})$ and *h* is the Planck constant $(6.626 \times 10^{-34} \text{ J} \cdot \text{s})$. The values of critical temperature of thermal explosion and the thermodynamic parameters are shown in table 3.

The corresponding critical temperatures of thermal explosion (T_b) for **1** and **2** are calculated as 218.7 and 263.4 °C, respectively. The value of critical temperature of thermal explosion for **2** was higher than that of **1** which indicated that **2** has better thermal stability.

4. Conclusion

Two new coordination compounds that use Li⁺ and Zn²⁺ as central ions and 3,4-amino-1,2,4triazolium as outer cation were synthesized and characterized. X-ray single-crystal structures of **1** and **2** were obtained. Li⁺ in **1** is coordinated by five oxygens (four from two TNR²⁻ anions and one from water), whereas in **2**, Zn²⁺ coordinates with three Cl⁻ and one nitrogen of DATr. The results from the DSC of these compounds indicated that they undergo one endothermic stage and one exothermic stage. The non-isothermal kinetic analyses indicate that the Arrhenius equation can be expressed as $\ln k = 9.135 - 109.8 \times 10^3 / (RT)$ (for **1**), $\ln k = 12.65 - 16.0 \times 10^3 / (RT)$ (for **2**). The values of critical temperature of thermal explosion ΔH^{\neq} , ΔG^{\neq} and ΔS^{\neq} are 104.41 J·K⁻¹·mol⁻¹, 189.54 kJ·mol⁻¹, -173.12 kJ·mol⁻¹ for **1**; and 157.94 J·K⁻¹·mol⁻¹, 235.60 kJ·mol⁻¹, -144.62 kJ·mol⁻¹ for **2**.

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Complex	1	2
Empirical formula	$C_{16}H_{22}Li_2N_{16}O_{20}$	$C_4H_{11}N_{10}Cl_3Zn$
Formula mass	772.38	370.97
Temperature (K)	153(2)	153(2)
Crystal system	Triclinic	Orthorhombic
Space group	<i>P</i> -1	Pna2(1)
Ζ	1	12
<i>a</i> (Å)	6.974(2)	12.035(3)
<i>b</i> (Å)	8.851(3)	7.0793(17)
<i>c</i> (Å)	12.487(4)	15.505(4)
α (°)	90.239(5)	90
β (°)	104.528(4)	90
γ (°)	95.036(5)	90
$V(\text{\AA}^3)$	742.9(4)	1321.0(6)
$D_c (g \cdot cm^{-3})$	1.726	1.865
$\mu(\mathrm{M}_{\mathrm{o}}K_{\alpha}) \ (\mathrm{mm}^{-1})$	0.157	2.466
F(000)	396	744
$\theta(^{\circ})$	2.824~31.482	3.16 ~ 31.50
Reflection measured	9939	11206
Independent reflection [R _{int}]	4800 [<i>R</i> _{int} =0.0244]	$4112[R_{int}=0.0354]$
S	1.003	1.003
$R_1, wR_2[I > 2\sigma(I)]$	0.0426, 0.1010	0.0347, 0.0588
$R_1, wR_2(all)$	0.0564, 0.1086	0.0395, 0.0609
$\Delta \rho_{\rm max}, \Delta \rho_{\rm min} ({\rm e} \cdot {\rm \AA}^{-3})$	-0.440, 0.526	0.504, -0.570

Table 1. Crystal data and structure refinement parameters for $(DATr)_2[Li_2(TNR)_2\cdot 2H_2O]\cdot 2H_2O$ (1) and $(DATr)[Zn(DATr)Cl_3]$ (2).

			1	2
		5	221.1	294.5
	$T_p(^{\circ}C)$	10	230.5	306.3
		15	240.7	310.2
		20	245.5	317.6
	Kissinger's	method		
	E _K [kJ∙	mol ⁻¹]	108.5	162.4
	$ln A_k$		9.135	12.65
	R _K		-0.9912	-0.9909
	Ozawa's m	ethod		
	$E_{\rm O}[{ m kJ}\cdot$	mol^{-1}]	111.1	163.6
	$R_{\rm O}$		-0.9925	-0.9919
P-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C))			

Table 2. Peak temperatures of the first exothermic stage at different heating rates and the kinetic parameters of **1** and **2**.

Compound	<i>T_{P0}</i> (°C)	<i>T_{bp}</i> (°C)	ΔH^{\neq} (kJ·mol ⁻¹)	ΔG^{\neq} (kJ·mol ⁻¹)	$\frac{\varDelta S^{\neq}}{(\mathbf{J} \cdot \mathbf{K}^{-1} \cdot \mathbf{mol}^{-1})}$
1	218.7	238.3	104.41	189.54	-173.12
2	263.4	279.36	157.94	235.60	-144.62

Table 3. Calculated critical temperature of thermal explosion and the thermodynamic parameters.

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Figure 1. Molecular structure of $(DATr)_2[Li_2(TNR)_2 \cdot 2H_2O] \cdot 2H_2O$.





Figure 3. Molecular structure of (DATr)[Zn(DATr)Cl₃].



Figure 4. Packing plots of [Zn(DATr)Cl₃](DATr).



Figure 5. DSC curves of **1** (a) and **2** (b) at a heating rate of 10 $^{\circ}C \cdot \min^{-1}$

