Relationship between Lattice Energy and Sensitivity of $[M(CHZ)_3](NO_3)_2$ and $[M(CHZ)_3](ClO_4)_2(M = Mn，Zn，Ni)$

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Abstract：The standard molar enthalpies of series of energetic coordination compounds solution with carbohydrazide as ligand and nitrate or perchlorate as anion in deionized water were measured by a Setaram C80Ⅱ microcalorimeter at 298. 15 K. Based on these values，their lattice energy were calculated through Kapustinkii formula，meanwhile the thermochemistry radius of $[M(CHZ)_3]^{2+}$（M = Mn，Zn，Ni）was gained. The relationship between lattice energy and impact sensitivity or friction sensitivity was discussed. Results show that the lattice energy of perchlorate are smaller than their corresponding nitrate，thus the perchlorate are more sensitive.

Key words：physical chemistry；$[M(CHZ)_3](NO_3)_2$；$[M(CHZ)_3](ClO_4)_2$（M = Mn，Zn，Ni）；enthalpy of solution；lattice energy；sensitivity

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1 Introduction

Carbohydrazide（CHZ）is a hydrazine derivative with white crystal of strong reducibility. Because it has many coordination atoms（four nitrogen atoms and one oxygen atom），carbohydrazide can，therefore，be used as multidentate ligand. Its coordination compound is widely used in the field of medicine，petroleum，national defense and energetic materials and so on[1]. In recent years，carbohydrazide energetic coordination compounds have received extensive attentions due to their potential properties such as good fluidity and lower sensitivities[2-4]. They can be used not only in weapon system as explosives or initiating explosives，but also in propellants as energetic catalysts. ZHANG Tong-lai，MA Gui-xia et al[5-6] have prepared a series of energetic coordination compounds with carbohydrazide as ligand and nitrate or perchlorate as anion and studied on their thermal decomposition and explosive properties. In order to research dissolution property，the enthalpies of solution of $[M(CHZ)_3](NO_3)_2$ and $[M(CHZ)_3](ClO_4)_2$（M = Mn，Zn，Ni）were measured by microcalormeter. Based on this，the standard molar enthalpies of solution and lattice energies of these coordination compounds were calculated and the influence of lattice energy on sensitivity was discussed.

2 Experimental

2.1 Reagents and apparatus

Manganese carbonate，basic nickel carbonate，basic zinc carbonate，manganese nitrate，nickel nitrate，zinc nitrate and perchloric acid were standard analytical pure. Carbohydrazide was prepared by the reference ways[7]. Samples of $[M(CHZ)_3](NO_3)_2$ and $[M(CHZ)_3](ClO_4)_2$ were synthesized according to the previous methods[5-6].

The calorimetric experiment was performed by using a Calvet microcalorimeter，type C80Ⅱ from Setaram，France.

2.2 Experiment and methods

The experimental precision and accuracy of the microcalorimeter was firstly checked by measurement of the enthalpies of solution of crystalline KCl（special purity）in deionized water at 298. 15 K. The experimental value（17. 232 ± 0. 052）kJ · mol^{-1} was in excellent agreement with that of（17. 241 ± 0. 018）kJ · mol^{-1}[8]. The accuracy was less than 0. 1%，which indicated that the calorimetric system was accurate and reliable.

In this experiment，a stainless steel mixing with membrane vessel was used，which had two compartments. The lower recipient was used to contain the deionized water and was closed by the membrane made of polytetrafluoroethylene（PTFE）. The upper container of the measure cell contained the known amount of $[M(CHZ)_3](NO_3)_2$ or

[M(CHZ)$_3$](ClO$_4$)$_2$. The measure and reference cells were placed inside a metallic block of the Calvet-type microcalorimeter. When thermal equilibrium was reached, the components in the vessels were mixed by piercing the membrane with a rod. Then the differential heat-flux was recorded.

The standard dissolution curves of [M(CHZ)$_3$](NO$_3$)$_2$ and [M(CHZ)$_3$](ClO$_4$)$_2$ are presented in Fig 1, which indicating that these reactions are totally endothermic. And the curves at other different concentrations are similar in tendency. Due to the molar ratio of deionized water to products was about 2.5×10^3 in experiment, the system could be regarded as infinite diluted solution and the standard molar enthalpy could be considered as the dissolution enthalpy. The enthalpies of solution and standard molar enthalpies of this series of coordination compounds are given in Table 1. The enthalpy of solution were obtained by the least square method based on seven groups of experimental data, which had the minimum error.
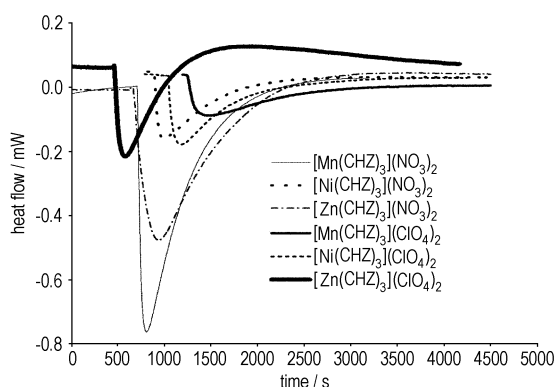

Fig.1　The standard dissolution curves
of [M(CHZ)$_3$](NO$_3$)$_2$ and [M(CHZ)$_3$](ClO$_4$)$_2$

Table 1　The standard molar enthalpies of solution
of [M(CHZ)$_3$](NO$_3$)$_2$ and [M(CHZ)$_3$](ClO$_4$)$_2$

complex	M / g · mol^{-1}	$\Delta_{sol}H$ / J · g^{-1}	$\Delta_{sol}H_m^\theta$ / kJ · mol^{-1}	SD
[Mn(CHZ)$_3$](NO$_3$)$_2$	449.19	202.86	91.13	0.00127
[Mn(CHZ)$_3$](ClO$_4$)$_2$	524.09	166.17	87.09	0.00084
[Ni(CHZ)$_3$](NO$_3$)$_2$	452.95	82.53	37.38	0.00049
[Ni(CHZ)$_3$](ClO$_4$)$_2$	527.85	165.43	87.32	0.00116
[Zn(CHZ)$_3$](NO$_3$)$_2$	459.64	156.96	72.15	0.00304
[Zn(CHZ)$_3$](ClO$_4$)$_2$	534.54	75.81	40.52	0.00020

Note：M, molecular weight; $\Delta_{sol}H$, dissolution enthalpy; $\Delta_{sol}H_m^\theta$, standard molar enthalpy of dissolution; SD, standard deviation.

3　Results and discussion

According to the structure of coordination com-

pounds, lattice energy is the energy change from the crystal salt to cation and anion[9], Which is obtained by the following equations：

$$[ML_n]X_m(cr) \xrightarrow{U} [ML_n]^{m+}(g) + mX^-(g) \quad (1)$$

$$U = \Delta_f H_m^\theta([ML_n]^{m+},g) + m\Delta_f H_m^\theta(X^-,g) - \Delta_f H_m^\theta([ML_n]X_m,cr) \quad (2)$$

where U is the lattice energy of complex, kJ · mol^{-1}; $\Delta_f H_m^\theta([ML_n]^{m+},g)$, $\Delta_f H_m^\theta(X^-,g)$ and $\Delta_f H_m^\theta([ML_n]X_m,cr)$ is the standard molar enthalpy of formation of cation and anion in gas phase, crystal complex respectively, kJ · mol^{-1}.

Owing to the difficulty of measuring the formation enthalpy of ions in gas phase directly in mostly situations, Kapustinkii experiential formula[9] is used to calculate lattice energy：

$$U = 1201.6 \frac{\eta_1 \eta_2 \sum n}{r_1 + r_2}(1 - \frac{0.345}{r_1 + r_2})kJ · mol^{-1} \quad (3)$$

Where U is the lattice energy, η_1 and η_2 are the cation and anion charges, $\sum n$ is the number of ions in the molecule, r_1 and r_2 are the moduli of radii of cation and anion.

In order to solve the problem of calculating the radii of non-global ion difficultly, a hypothesis about the thermochemistry radius was put forward, which was a assumed radii of global ion instead of that of non-global ion equally in crystal lattice. Based on this theory, the different formation energy or lattice energy between two coordination compounds with the same cation or anion is determined by different counterions. Therefore, according to the enthalpy of solution, lattice energy of complex in calculated by following equations. The dissolution in water of complex is regarded as：

$$[ML_n](X)_m(cr) \xrightarrow{\Delta_{sol}^1 H_m^\theta} [ML_n]^{m+}(aq,\infty) + mX^-(aq,\infty) \quad (4)$$

$$[ML_n](Y)_m(cr) \xrightarrow{\Delta_{sol}^2 H_m^\theta} [ML_n]^{m+}(aq,\infty) + mY^-(aq,\infty) \quad (5)$$
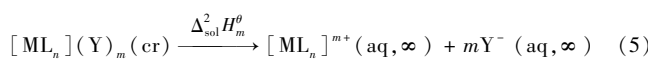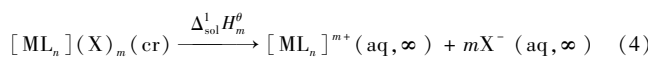
Where $[ML_n]^{m+}$ is the complex ion, X^- and Y^- are counterions. According to equation (4) and (5), the standard formation enthalpy of complex was obtained by the following equations：

$$\Delta_f H_m^\theta \{ [ML_n](X)_m,cr,298.15 \ K \} = \Delta_f H_m^\theta([ML_n]^{m+},aq,\infty) + m\Delta_f H_m^\theta(X^-,aq,\infty) - \Delta_{sol}^1 H_m^\theta \quad (6)$$

$$\Delta_f H_m^\theta \{ [ML_n](Y)_m,cr,298.15 \ K \} = \Delta_f H_m^\theta([ML_n]^{m+},aq,\infty) + m\Delta_f H_m^\theta(Y^-,aq,\infty) - \Delta_{sol}^2 H_m^\theta \quad (7)$$

Taking [Ni(CHZ)$_3$](NO$_3$)$_2$ and [Ni(CHZ)$_3$](ClO$_4$)$_2$

for an example, combined with equation (2) and (3), $[ML_n]^{m+} = [Ni(CHZ)_3]^{2+}$, $X^- = NO_3^-$, $Y^- = ClO_4^-$, the different value between them was calculated:

$$U_{[Ni(CHZ)_3](NO_3)_2} - U_{[Ni(CHZ)_3](ClO_4)_2} = 2\Delta_f H_m^\theta(NO_3^-,g) -$$

$$2\Delta_f H_m^\theta(NO_3^-,aq,\infty) + 2\Delta_f H_m^\theta(ClO_4^-,aq,\infty) - 2\Delta_f H_m^\theta(ClO_4^-,g) +$$

$$\Delta_{sol}H_m^\theta([Ni(CHZ)_3](NO_3)_2) - \Delta_{sol}H_m^\theta([Ni(CHZ)_3](ClO_4)_2) =$$

$$1201.6 \frac{\eta_1\eta_2\sum n}{r_{[Ni(CHZ)_3]^{2+}} + r_{NO_3^-}}(1 - \frac{0.345}{r_{[Ni(CHZ)_3]^{2+}} + r_{NO_3^-}}) -$$

$$1201.6 \frac{\eta_1\eta_2\sum n}{r_{[Ni(CHZ)_3]^{2+}} + r_{ClO_4^-}}(1 - \frac{0.345}{r_{[Ni(CHZ)_3]^{2+}} + r_{ClO_4^-}})$$

By substituting the following data into the equation above.

$\Delta_f H_m^\theta(NO_3^-,g) = -336.0$ kJ · mol^{-1};

$\Delta_f H_m^\theta(NO_3^-,aq,\infty) = -205.0$ kJ · mol^{-1};

$\Delta_f H_m^\theta(ClO_4^-,g) = -384.3$ kJ · mol^{-1};

$\Delta_f H_m^\theta(ClO_4^-\ aq,\infty) = -129.33$ kJ · mol^{-1};

$\Delta_{sol}H_m^\theta([Ni(CHZ)_3])(NO_3)_2) = 37.38$ kJ · mol^{-1};

$\Delta_{sol}H_m^\theta([Ni(CHZ)_3])(ClO_4)_2) = 87.32$ kJ · mol^{-1};

$r_{NO_3^-} = 1.65$ Å; $r_{ClO_4^-} = 2.36$ Å

The radius of complex ion ($[Ni(CHZ)_3]^{2+}$) is calculated to be 2.70 Å. By substituting the value $r_{[Ni(CHZ)_3]^{2+}} = 2.70$ Å into equation (3), the lattice energy is gained: $U_{[Ni(CHZ)_3](NO_3)_2} = 1525.93$ kJ · mol^{-1}, $U_{[Ni(CHZ)_3](ClO_4)_2} = 1327.68$ kJ · mol^{-1}

Also the other radii and lattice energy is obtained, the radius of complex ion of $[Mn(CHZ)_3]^{2+}$ and $[Zn(CHZ)_3]^{2+}$ is 2.12 Å and 1.89 Å, respectively. For observing the relationship between the lattice energy and sensitivity, the values are listed in Table 2.

Table 2 The lattice energy and sensitivity of
$[M(CHZ)_3](NO_3)_2$ and $[M(CHZ)_3](ClO_4)_2$

complex	$\Delta_{sol}H_m^\theta$ /kJ · mol^{-1}	U /kJ · mol^{-1}	P /%	H_{50} /cm
$[Mn(CHZ)_3](NO_3)_2$	91.13	1737.36	60	no firing at 50
$[Mn(CHZ)_3](ClO_4)_2$	87.09	1485.36	58	23.7
$[Ni(CHZ)_3](NO_3)_2$	37.38	1525.93	24	30
$[Ni(CHZ)_3](ClO_4)_2$	87.32	1327.68	80	12.47
$[Zn(CHZ)_3](NO_3)_2$	72.15	1838.13	0	no firing at 50
$[Zn(CHZ)_3](ClO_4)_2$	40.52	1558.67	34	23.35

Note: U, lattice energy; P, firing percent of friction sensitivity in condition of 20 mg complexes and the 800 mg switching hammer; H_{50}, height for 50% probability of ignition of impact sensitivity in condition of the same quantity of complexes and the dropping hammer respectively with that in P.

It appears that the lattice energy of $[M(CHZ)_3](NO_3)_2$ is totally larger than that of their corresponding $[M(CHZ)_3](ClO_4)_2$. The reason is that the radius of NO_3^- in gas phase is 1.65 Å, while ClO_4^- is 2.36 Å, so the interaction force between center ion and outside ion is lower. In series of nitrate and perchlorate, the compound with zinc as center ion is highest in terms of lattice energy, while nickel is lowest, which maybe concerned with metal coordinated states and its own property. Also, even if the lattice energy is close, the sensitivity is still widely different. That's because the sensitivity is a complex parameter, not only related to lattice energy, but also other factors.

4 Conclusion

The standard molar enthalpies of solution of $[M(CHZ)_3](NO_3)_2$ and $[M(CHZ)_3](ClO_4)_2$ were measured by a Setaram C80II microcalorimeter in deionized water at 298.15 K and their lattice energies were calculated, while the thermochemistry radius of $[M(CHZ)_3]^{2+}$ was gained. The larger the lattice energy is, the more insensitive the complex is, no matter what the friction sensitivity or impact sensitivity is. The highest sensitive compound is $[Ni(CHZ)_3](ClO_4)_2$ and the most insensitive is $[Zn(CHZ)_3](NO_3)_2$, which is not only related to their lattice energy, but also possibly concerned with states of metal coordination and metal property. These would establish basal data for further research.

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高氯酸碳酰肼盐与硝酸碳酰肼盐系列化合物的晶格能与感度性能关系

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摘要：为了研究晶格能与感度之间的关系，采用微热量计测定了［M（CHZ）₃］（NO₃）₂ 和［M（CHZ）₃］（ClO₄）₂（M = Mn，Zn，Ni）在去离子水中的溶解焓并计算出它们的标准摩尔溶解焓，根据卡普廷斯基经验公式计算了它们的晶格能，得出配阳离子半径［M（CHZ）₃］²⁺（M = Mn，Zn，Ni）分别为 2.12Å，1.89Å 和 2.70Å；讨论了晶格能与机械感度之间的关系：相同外阴离子系列中配合物的晶格能越大，感度越小，并且高氯酸碳酰肼盐要比相应的硝酸碳酰肼盐的晶格能低，感度最高的为［Ni（CHZ）₃］（ClO₄）₂，最钝感的为［Zn（CHZ）₃］（NO₃）₂。

关键词：物理化学；［M（CHZ）₃］（NO₃）₂；［M（CHZ）₃］（ClO₄）₂（M = Mn，Zn，Ni）；溶解焓；晶格能；感度

Synthesis and Blending of High-density Hydrocarbon Fuels with Density Beyond 1.0 g · cm⁻³

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Abstract：Three high-density hydrocarbons with molecular structure of $C_{10}H_{16}$（C10），$C_{15}H_{22}$（C15）and $C_{20}H_{28}$（C20）were synthesized using dicyclopentadiene as feedstocks. The density of the fuels increases in the order of C10，C15 and C20，whereas the low-temperature properties show the inverse tendency. To obtain higher density and acceptable low-temperature property，binary and ternary blendings of them were prepared. The dependence of density and viscosity on the composition of blends was analyzed，and an equation was established to predict the density of blendings. C10 can improve the low-temperature of blendings，whereas C20 can enhance the density. According to the density-viscosity-composition ternary diagrams，an optimized blending composition of C15⩾75wt%，C20⩽20wt% and C20⩽5wt% was determined. The resulting fuel has density larger than 1.0 g · cm⁻³（15 ℃），volume heat larger than 42.0 MJ · L⁻¹，viscosity smaller than 500 mm² · s⁻¹（－40 ℃），and pour point smaller than －70 ℃，which is very promising for propulsion applications.

Key words：organic chemical engineering；high-density hydrocarbon；aviation fuel；dicyclopentadiene；blending fuel