

1, 3-二硫杂环戊烯-2-硫酮-4, 5-二巯基的不对称二硫纶金属(Cd, Zn)
配合物的热行为 and 热分解反应动力学陆振荣^{*1} 丁元晨¹ 徐颖¹ 戴洁²¹ 苏州大学分析测试中心, 苏州 215006)² 苏州大学化学化工系, 苏州 215006)

用 TG-DTG-DTA 联用技术研究了两种 1, 3-二硫杂环戊烯-2-硫酮-4, 5-二巯基的不对称二硫纶金属(Cd, Zn)配合物在动态氮气气氛中的热行为, 通过应用 EDS 技术和元素分析方法对热分解过程中各步反应中间体的组成进行了探索, 并结合其物质结构进行了讨论。协同使用四种热分析动力学方法获得了各步反应的热分解动力学参数, 并推断了它们的最可能分解反应机理。

关键词: 镉配合物 锌配合物 苯硫酚基 热分析

1, 3-二硫杂环戊烯-2-硫酮-4, 5-二巯基(dmit)

分类号: O613.51 O614.24*1 O614.24*2

Thermal Behavior and Decomposition Kinetics of Unsymmetrical Dithiolene
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TA study on two unsymmetrical dithiolene metal(Cd, Zn) complexes of 1, 3-dithiole-2-thione-4, 5-dithiolate (dmit) was carried out using a simultaneous TG-DTG-DTA technique in a dynamic nitrogen atmosphere and at various heating rates. Supplemented by using both EDS and elemental analysis methods, their thermal behavior and the composition of their intermediate products were examined and discussed in connection with their molecular structure. Four thermal analysis kinetic methods were jointly employed to calculate the non-isothermal kinetic parameters and to determine the most probable decomposition mechanisms.

Keywords: Cd complex Zn complex thiophenolate thermal analysis(TA)

1, 3-dithiole-2-thione-4, 5-dithiolate (dmit)

Research in metal bis-dithiolenes is of great interest over the past decades due to the fact that they not only can be used as materials of electrical conductors^[1, 2], but also exhibit unusual optical properties^[3]. They are known to be quite stable to intense irradiation

in the near-infrared region and have been used as Q-switch dyes for Nd: YAG lasers^[4]. Among them, in addition to a series of symmetrical complexes with third-order optical nonlinearity which have shown potential as materials for all-signal processing devices^[5],

收稿日期: 2003-03-12。收修改稿日期: 2003-06-04。

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some unsymmetrical dithiolene-metal complexes have recently been observed to possess large values of third-order nonlinear susceptibility^[6] as well as negative molecular first hyperpolarizability^[7]. So far as we know, however, there has been little study on their thermal properties which is actually very important for them to be better and more extensively used.

We^[8] have reported the preparation, crystal structure and third-order optical nonlinearity of two new unsymmetrical dithiolene metal (Cd, Zn) complexes of 1, 3-dithiole-2-thione-4, 5-dithiolate, $(Me_4N)_2[Cd(dmit)(Sph)_2]$ and $(Me_4N)_2[Zn(dmit)(Sph)_2]$ (where Me_4N = tetramethyl ammonium ion, $dmit$ = 1, 3-dithiole-2-thione-4, 5-dithiolate, Sph = thiophenolate group). In order to further investigate their properties and application, in this paper we studied them using TG-DTG-DTA technique and presented their thermal behavior, together with all the kinetic analysis results of their decomposition, such as the reaction mechanism and the Arrhenius parameters determined and calculated by jointly using several data processing approaches. Meanwhile, we also discussed the relationship between their structure and thermal properties.

1 Experimental

1.1 Material

The compounds studied were synthesized by the method described in our previous paper^[8]. All the chemicals used in the synthesis were Analar grade. Their compositions were confirmed by elemental analysis and the quality of sample for TA study was identified with that of the samples for single crystal XRD study^[8].

1.2 Apparatus and Methods

Thermal experiments were performed in a SDT 2960 DTA-TGA (TA Instruments). This apparatus allows TG and DTA measurements to be taken simultaneously^[9]. Crucibles were made from alumina. The instrument was previously calibrated against standard substances provided by TA Instruments. All the tests were carried out under non-isothermal conditions at different heating rate (β) of 5, 10, 15 and 20°C ·

min⁻¹ respectively, in flowing (100mL · min⁻¹) nitrogen of 99.99% using samples within the range 5 ~ 10mg which were gently crushed with a pestle and mortar before measured. Simultaneous TG-DTG-DTA curves were obtained in the range 50 ~ 900°C.

Carlo-Erba model 1110 elemental analyzer and the energy-dispersive spectrometer (EDS), EDAX PV9900 were employed to check the composition for both intermediates and residues^[9, 10].

2 Kinetic methods

In view of general complexity in the processes involved in solid-state reactions^[11-14], several thermal analysis kinetic (TAK) methods were jointly employed in this paper to process the TG-DTG data to determine the decomposition mechanisms and to calculate the Arrhenius parameters, i. e. the activation energy E and the pre-exponential factor A for the compounds studied. These methods are as follows:

2.1 Single Scanning Methods

Achar-Brindly-Sharp (A-B-S) equation:

$$\ln \left[\frac{1}{f(\alpha)} \frac{d\alpha}{dt} \right] = \ln A - \frac{E}{RT} \quad (1)$$

Coats-Redfern (C-R) equation:

$$\ln \left[\frac{g(\alpha)}{T^2} \right] = \ln \left[\left(\frac{AE}{\beta R} \right) \left(1 - \frac{2RT}{E} \right) \right] - \frac{E}{RT} \quad (2)$$

2.2 Multiple Scanning Methods

Kissinger equation:

$$\ln \left(\frac{\beta}{T_p^2} \right) = \ln \frac{AR}{E} - \frac{E}{RT_p} \quad (3)$$

Flynn-Wall-Ozawa (F-W-O) equation:

$$\lg \beta = \lg \left(\frac{AE}{Rg(\alpha)} \right) - 2.315 - 0.4567 \frac{E}{RT} \quad (4)$$

Since the above equations and the symbols in them are those in common use, we omit their references and annotation to save space.

As the two multiple scanning methods, i. e. Kissinger and Flynn-Wall-Ozawa equations, are model-free isocoverisional methods and allow the activation energy to be independently obtained, the E values calculated using them were used to check the constancy and validity of activation energy by the other methods.

3 Results and Discussion

3.1 Thermal Behavior

Thermal analytical data measured at $\beta = 5\text{K} \cdot \text{min}^{-1}$ for the complexes are listed in Table 1. The percentage mass loss and the probable composition of the expelled groups are also given. The TG-DTG and DTA curves at a heating rate of $5\text{K} \cdot \text{min}^{-1}$ for both complexes are presented in Fig. 1 and 2, respectively. Besides, in order to make discussion clearer, it seems helpful to recollect both the main part of molecular structure and some useful crystal structure data of these complexes which have been studied by XRD and reported in our previous paper^[8] and here showed in Fig. 3.

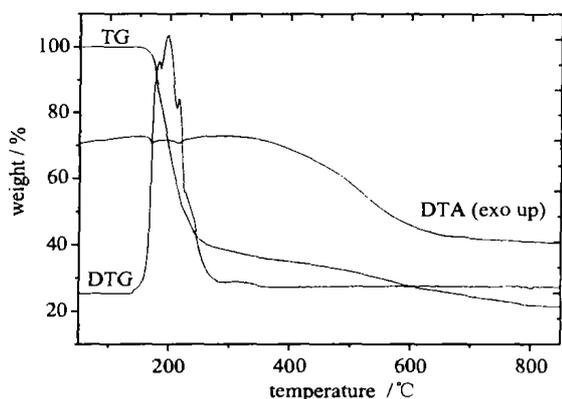


Fig. 1 TG-DTG-DTA curve of $(\text{Me}_4\text{N})_2[\text{Cd}(\text{dmit})(\text{Sph})_2]$

As seen from Table 1 and Fig. 1, the Cd complex shows a three-step decomposition mode but without any stable intermediate formed. The mass loss percentage suggests that the probable expelled group for the first stage is two Me_4N , then followed by the evolution of the dmit. The third stage corresponds to the simultaneous

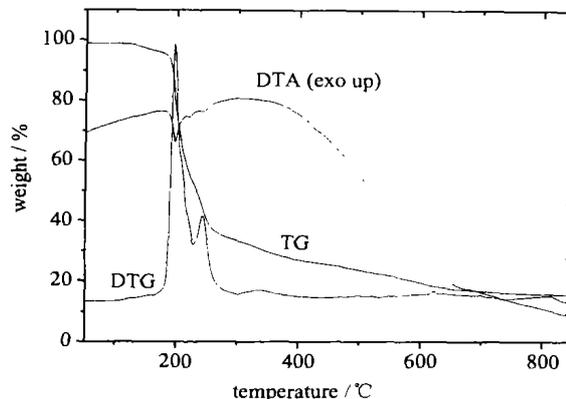


Fig. 2 TG-DTG-DTA curve of $(\text{Me}_4\text{N})_2[\text{Zn}(\text{dmit})(\text{Sph})_2]$

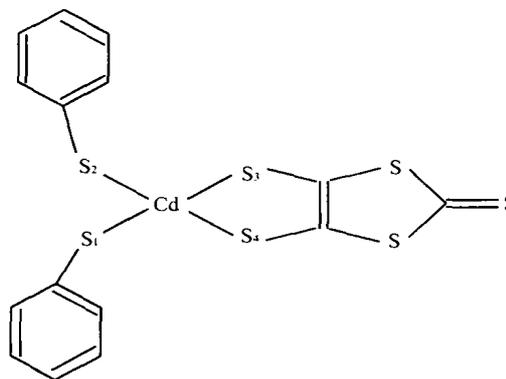


Fig. 3 Schematic drawing of $(\text{Me}_4\text{N})_2[\text{Cd}(\text{dmit})(\text{Sph})_2]^{2-}$

removal of two thiophenolate moieties. This was confirmed by an analysis of the intermediate products of the complex isolated immediately after the first and the second stage respectively using a Carlo-Erba model 1110 elemental analyzer, which shows that there is no nitrogen left in the intermediate at the end of the first decomposition stage and that, on the other hand, there is hydrogen still remained in that after the second stage. The mass loss and the elemental analysis using EDS indicate that the final residue is CdS. Fig. 4 gives

Table 1 Thermal Decomposition Data for $(\text{Me}_4\text{N})_2[\text{Cd}(\text{dmit})(\text{Sph})_2]$ and $(\text{Me}_4\text{N})_2[\text{Zn}(\text{dmit})(\text{Sph})_2]$ under an Atmosphere of Dynamic Nitrogen ($\beta = 5\text{K} \cdot \text{min}^{-1}$)

complex ^a	temp. range/°C	DTG peak temp. /°C	loss of mass/%		probable composition of expelled groups ^b	
			obs.	theory		
Cd complex	I	148 ~ 186	179	0.2203	0.2195	2Me ₄ N
	II	186 ~ 218	197	0.2427	0.2432	dmit
	III	218 ~ 839	227	0.3237	0.3233	2Sph
Zn complex	I	131 ~ 228	196	0.5078	0.4973	2Me ₄ N, dmit
	II	228 ~ 815	242	0.3321	0.3475	2Sph

Note: a: $(\text{Me}_4\text{N})_2[\text{Cd}(\text{dmit})(\text{Sph})_2]$ and $(\text{Me}_4\text{N})_2[\text{Zn}(\text{dmit})(\text{Sph})_2]$; b: Me₄N = tetramethyl ammonium ion, dmit = 1,3-dithiole-2-thione-4,5-dithiolate, Sph = thiophenolate group

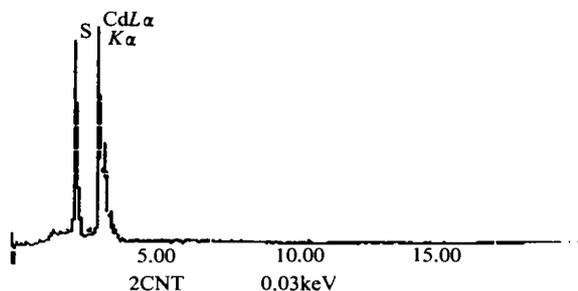


Fig. 4 EDS analysis for the residue of $(\text{Me}_4\text{N})_2[\text{Cd}(\text{dmit})(\text{Sph})_2]$

the result for Cd complex.

This behavior is expected from chemical consideration. As compared with the ligand, either dmit or thiophenolate group, which coordinates to Cd through S atom of stronger electronegativity, Me_4N , as a cation group, combines with the whole complex ion and is thus easier to decompose. As to the two ligands, although dmit is a strong chelate ligand, the thiophenolate group also coordinates strongly to the metal center^[8]. In fact, during the synthesis of these complexes by the cluster-cracking reaction of $(\text{dmit})^{2-}$ with $[\text{M}_4(\text{Sph})_{10}]^{2-}$ (where $\text{M} = \text{Cd}$ or Zn), it was found that unlike chloride ion, which is easily displaced by dmit, the thiophenolate resists displacement and thus the mixed ligand complexes like these studied in the present work were formed. X-ray structure determination^[8] reveals that the bond distances Cd to the sulfur of dmit, $\text{Cd-S}(3) = 0.2530(2)$ nm, $\text{Cd-S}4 = 0.2566(2)$ nm, are even longer than that of Cd to the sulfur of the thiophenolate group, $\text{Cd-S}(1) = 0.2507(1)$ nm, $\text{Cd-S}(2) = 0.2519(2)$ nm (See Fig. 3), which can be explained by its rigid structure, because the $\text{S}(3)-\text{Cd-S}(4)$ angle of $88.72(5)^\circ$ deviates significantly from the 109° of a tetrahedron; while the monodentate ligand thiophenolate coordinates without any bond strain, the $\text{S}(1)-\text{Cd-S}(2)$ angle is just $110.77(6)^\circ$. That is the reason not only the thiophenolate group is not fully replaced during the synthesis, but also its decomposition occurs after dmit during heated.

DTA curve for the Cd complex shows two weak endothermic peaks and their peak temperatures are quite close to that of the first and the second stage in

DTG curve, respectively.

The Zn complex exhibits a similar decomposition pattern except the fact that its first and second decomposition stages take place so continuously that its whole decomposition process appears a only two-step mode, even at a low heating rate which is believed to be helpful to reveal the nature and details of competitive and independent reaction concurrently proceeded. Relevantly, the DTA curve of Zn complex shows only one endothermic peak.

3.2 Thermal Decomposition Kinetics

Table 2 presents the basic data, β , T_p , obtained from TG-DTG curves which were used to calculate the activation energy E by both F-W-O and Kissinger equation. Using the data, α , T and $d\alpha/dT$ from TG-DTG curves and 43 commonly used kinetic mechanism functions of $f(\alpha)$ and $g(\alpha)$ ^[15], the kinetic parameters E , $\lg A$ and appropriate linear coefficients r and standard deviation (S. D.) values were calculated by both A-B-S and C-R equation with the linear least squares method. The most probable mechanism for each decomposition stage was determined following the commonly employed method: The values of E and $\lg A$ obtained by the two methods must not only be approximately equal and but also correspond to a higher linear correlation coefficient and a lower standard deviation; meanwhile, the E value calculated using both Kissinger and F-W-O equations were used for checking their reasonableness as multiple scanning methods are considered be able to get more reasonable activation energy E .

Table 2 Peak Temperature T_p of DTG Curves at Various Heating Rates β

complex*	stage	$\beta / (\text{K} \cdot \text{min}^{-1}) (T_p / ^\circ\text{C})$			
Cd complex	I	5(179)	10(190)	15(199)	20(207)
	II	5(197)	10(207)	15(215)	20(221)
	III	5(227)	10(241)	15(247)	20(252)
Zn complex	I	5(196)	10(202)	15(208)	20(213)
	II	5(242)	10(256)	15(262)	20(267)

* The same as the note to Table 1.

The kinetic parameters, E and $\lg A$ together with their appropriate linear correlation coefficient r and

Table 3 Kinetic Parameters of Thermal Decomposition for both Cd and Zn Complex

complex ^a	method ^b	$E/(kJ \cdot mol^{-1})$	$lg A$	r^c	S. D. ^d	
Cd complex	I	Kissinger	81.79	7.076	0.9928	0.08055
		F-W-O	85.14	—	0.9941	0.03474
	II	Kissinger	103.3	9.164	0.9964	0.05789
		F-W-O	105.8	—	0.9969	0.02498
	III	Kissinger	109.5	9.077	0.9961	0.06022
		F-W-O	112.2	—	0.9966	0.02627
Zn complex	I	Kissinger	144.1	13.91	0.9875	0.1101
		F-W-O	144.6	—	0.9888	0.04772
	II	Kissinger	119.2	9.726	0.9965	0.0575
		F-W-O	121.7	—	0.9969	0.02510

a: The same as the notes to Table 1; b: F-W-O, Flynn-Wall-Osawa; c: Linear coefficient;

d: Standard deviation

S. D., obtained from the two multiple scanning methods for both complexes studied are summarized in Table 3. It can be seen that the E values by these two methods are not only in a relatively good agreement, but also corresponding to quite ideal r and S. D. values except that for the first decomposition stage of Zn complex which is actually a partly overlapped each other by the removal of both Me_4N and dmit.

Jointly determined by the four methods used in the present work, the decomposition of Me_4N for Cd complex is controlled by reaction order equation R2, $f(\alpha) = (1 - \alpha)^2$, with E about $83kJ \cdot mol^{-1}$; while that of dmit is governed by JMA equation, $f(\alpha) = 3(1 - \alpha) [-\ln(1 - \alpha)]^{2/3}$ with E about $104kJ \cdot mol^{-1}$. The last stage for both complexes obeys the Jander equation, $f(\alpha) = 3(1 - \alpha)^{2/3}/2[1 - (1 - \alpha)^{2/3}]$, with E ranging $110 \sim 122kJ \cdot mol^{-1}$. As the first decomposition stage of Zn complex shows a quite strong dependence of E on the conversion α and it is a multiple stage, its kinetic mechanism is thus considered non-significant^[10, 11].

References

[1] Cassoux P., Valade L., Kobayashi A. et al *Coord. Chem. Rev.*, **1991**, **110**, 115.

- [2] Pullen A. E., Olk R. M. *Coord. Chem. Rev.*, **1999**, **188**, 211.
- [3] Mueller-Westerhoff U. T., Vanace B., Yoon D. I. *Tetrahedron*, **1991**, **47**, 909.
- [4] Recynolds G. A., Drexhage K. H. *J. Appl. Phys.*, **1975**, **46**, 4852.
- [5] Ushijima H., Kawasaki T., Kamata T. et al *Mol. Cryst. Liq. Cryst.*, **1996**, **286**, 275.
- [6] Hill C. A. S., Charlton A., Underhill A. E. et al *J. Chem. Soc., Dalton Trans.*, **1995**, 587.
- [7] Cummings S. D., Cheng L. T., Eisenberg R. *Chem. Mater.*, **1997**, **9**, 195.
- [8] Dai J., Bian G. Q., Wang X. et al *J. Am. Chem. Soc.*, **2000**, **122**, 11007.
- [9] Lu Z., Ding Y., Xu Y. et al *J. Therm. Anal. Calor.*, **2002**, **70**, 985.
- [10] LU Zhen-Rong(陆振荣), DING Yuan-Chen(丁元晨), XU Ying(徐颖) et al *Wuji Huaxue Xuebao(Chinese J. Inorg. Chem.)*, **2002**, **18**(11), 1107.
- [11] Vyazovkin S. *Int. Reviews in Physical Chemistry*, **2000**, **19**, 45.
- [12] Sestak J., Malek J. *Solid State Ionics*, **1993**, **63 ~ 65**, 245.
- [13] Flynn J. H. *Thermochim Acta*, **1997**, **300**, 83.
- [14] LU Zhen-Rong(陆振荣) *Wuji Huaxue Xuebao(Chinese J. Inorg. Chem.)*, **1998**, **14**, 119.
- [15] HU Rong-Zu(胡荣祖), SHI Qi-Zhen(史启祯) *Thermal Analysis Kinetics(热分析动力学)*, Beijing: Science Press, **2001**, p127 ~ 131.