第1卷 第4期
1993年12月

含 能 材 料
ENERGETIC MATERIALS

Vol. 1, No. 4
December, 1993

SHORT COMMUNICATION

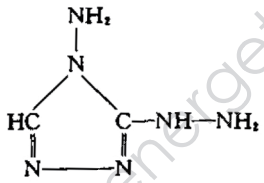
THE CORRELATION BETWEEN THERMAL DECOMPOSITION AND LASER IGNITION PARAMETERS FOR COMPLEXES OF HAT

Ilushin M A Petrova N A Tselinsky I V

(The St-Peterbug Institute of Technology, Russia)

HAT (4-amino-3(5)hydrazino-1,2,4-triazole) is of interest as reactive ligand for transitional metal complexes. Mass-spectral investigations of HAT show its molecular ion beging unstable (Table 1).

Table 1 Mass-spectral fragmentation of HAT

Ligand	*m/z*(% t.i.c)
 *M*=114	114(0.7); 99(0.7); 98(1.2); 97 (1.8); 84(2.6); 83 (1.9); 82(1.2); 81(1.6); 73(2.7); 67(12.1); 57(3.9); 56(1.1); 55(2.4); 43(1.9); 42(1.3); 41(2.9); 28(58.6)

The fragmentation of HAT proceeds via two main routes. The first route involes the elimination of RCN whereas the second path proceeds through a consecutive elimination of NH and NH_2 groups. The basic peak has the *m/z* ratio 28 (nitrogen or H_2CN). A relatively stable ion with the *m/z* ratio 67 is identified as triazole.

The reaction of complex formation of HAT with nitrates of Ag(Ⅰ), Ni(Ⅱ), Cu(Ⅱ) has been carried out in aqueous media[1,2]. The IR spectra of the complexes show that ligand coordination takes place via nitrogen electron pairs of the azole cycle. The amino group does not take place in the complex formation. The NO_3^- ion is located at the outer sphere of the nitrate complexes. The ESR spectrum of the HAT copper complex shows a symmetric singlet signal. This complex apper to have polymeric nature. HAT is a N,N-bidentate ligand, in which N(1) and N(2) atoms of the triazole cycle are coordinated.

1993年2月22日收稿

The thermal decomposition of the above nitrate complexes is found to be subject to metal cation catalysis. This conclusion is based on differential thermal analysis data (Table 2).

Table 2 Differential thermal analysis data of the HAT complexes at $V(t)=5K/min$

$[Cu(HAT)_2](NO_3)_2 \cdot H_2O$		$[Ni(HAT)_2](NO_3)_2$		$[Ag(HAT)](NO_3)$	
T/K	m/%	T/K	m/%	T/K	m/%
318～358[1)]	6.84	318～503	4.88	393	27.66
410	75.24	543	52.03	523	23.40
423～777	10.26	658	29.27	605	2.66
				693	10.11

1) endo-effect

The investigated complexes decompose with exo-effects. Cu(Ⅰ) cation appears to be the most effective catalyst of thermal decomposition.

The catalytic effect of metals in the thermal decomposition of the above complexes may have diverse applications. The possibility of the laser beam initiation is one way of application of HAT complexes.

Perchloric complexes of Cu(Ⅰ) and Ni(Ⅰ) with HAT as a ligand were synthesised and used as laser initiated mine explosives. This part of our work was performed in collaboration with Dr. Chernai A V (Institute of Mines, Ukraine, Dnepropetrovsk). The Nd-laser with the wavelength 1.06 μm and impulse time of 20 ns was used in the experiments. The Cu (Ⅰ) complex was found to require less laser energy (0.04J/cm²) for ignition than the Ni (Ⅰ) complex (more than 0.4J/cm²). This fact confirms the key role of a metal ion in the process of laser initiation.

The method of ballistic pendulum was used to study the explosive decomposition of the Cu(Ⅰ) complex. A simple equation describing the process was drawn:

$$J = (110.4 \pm 6.6)m - (1459.0 \pm 441.6) \qquad r = 0.99$$

Where J——impulse, dyne/cm² · s; m——mass of the sample, mg/cm²; r——correlation coefficient.

The equation shows that there exist a relation between the ignition ability and the thickness of the Cu(Ⅰ) complex sample.

EXPERIMENTAL

Here are given experimental conditions for differential thermal analysis of the salts: derivatography "Paulic E, Paulic J, Erdey L" (Hungary), the speed of heating 5K/min, the mass of a sample 10～20mg. IR spectra of complexes were recorded in Nujol on a "Brucker-IFS-113" spectrometer (Germany). Mass spectra of HAT were registrated on a MX-1310 spectrometer (USSR) under the electron energy of 70 eV. ESR spectra of polycrystalline samples of Cu complex at 297K were recorded on a P3-1306 spectrometer

(USSR). The samples of Cu complex of 1 cm in diameter were ignited by a Nd-laser ГОС-30М (USSR) which had special optic system for defocussing of the laser beam.

REFERENCES

1 Ilushin M A, Sokolov V M, Smirnov A V, Ivannikova T A. Polyazoles Complex Compounds as a Perspective Class in the Search of New Pesticides. The Third Regional Conference of the Middle Asian Republics and Kazakhstan on Chemical Reagents. Tashkent, October 1990. Inorganic and Bioorganic Reactives. 1990,2:8 (in Russian).

2 Ilushin M A, Smirnov A V, Vasiliev I P, Tselinsky I V. Synthesis and Biological Activity of New Biometal Azole Complexes. Abstracts of Reports 8th Conference (Intern.) of Young Scientists on Organic and Bioorganic Chemistry. Riga, November 2～9,1991. 73

向审稿者致谢

本刊自 1993 年 1 月创刊以来，承蒙各界许多同志帮助审阅了大量的稿件，使本刊得以顺利出版发行，为此，本编辑部特向下列各位审稿者（按汉语拼音为序）致谢！

陈博仁　陈启珍　陈学林　楚士晋　丁叔瀛　董海山　方宗蓥　耿春余
韩均万　郝　莹　胡荣祖　花平环　黄世伟　黄　涛　黄亦刚　李常青
李上文　梁香林　陆　明　吕春绪　阮庆云　舒远杰　松全才　谭显祥
唐兴初　王世昌　王士俊　王泽山　吴　雄　肖登达　肖鹤鸣　谢高弟
徐　康　杨克斌　游开兴　郁向东　云主惠　章冠人　张熙和　赵子敬
郑培森　朱春华　朱祖良

《含能材料》编辑部
一九九三年十二月