

Thermal behavior of various metal complex nitrates (1)

— Qualitative gas evolution behavior —

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Various metal complexes expected to be a new gas generant for automobile air bags were synthesized and their gas evolution behavior was investigated. The synthesized substances were the Zn complexes of hydrazine, semicarbazide, triaminoguanidine and urea and the Cu complex of aminoguanidine.

For the Zn complexes of hydrazine and triaminoguanidine and the copper complex of aminoguanidine, fragment number 28 (N₂) was mainly confirmed during the decomposition at a heating rate of 20 °C/min.

For the Zn complexes of semicarbazide and urea, mainly fragment number 44 (N₂O or NH₂CO) was confirmed. In the case of the copper complex of aminoguanidine and the Zn complex of triaminoguanidine, the evolution of cyan gas was suspected from the -C=N- bonding in the structure.

1. Introduction

Recently, an automobile sold in Japan has equipped with an airbag system for safer driving. A non-azide gas generant as a substitutes for sodium azide has been studied, and tetrazole derivatives¹⁾, urazole²⁾ and azodicarboamide³⁾ were the subjects of this study.

The authors evaluated the metal complexes of organic compounds, which are composed of a great deal of nitrogen atoms, as the new gas generant. In previous reports¹⁻⁹⁾, the thermal decomposition behavior of the metal complex of carbonylhydrazide was investigated.

In this report, the metal complex nitrates of hydrazine, semicarbazide, triaminoguanidine, aminoguanidine and urea were synthesized, and the gas evolution behavior was qualitatively investigated.

2. Experiment

2.1 Reagents

The metal nitrates and various ligands (Table 1)

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Table 1 lists of ligands

Hydrazine (NN) <chem>NH2NH2</chem>	Semicarbazide (SB) <chem>H2N-NH-C(=O)-NH2</chem>	Urea (UR) <chem>H2N-C(=O)-NH2</chem>
Triaminoguanidine (TAG) <chem>H2N-NH-C(=N)-NH2</chem>	Aminoguanidine (AG) <chem>H2N-C(=N)-NH2</chem>	

were Wako Pure Chemical reagent grade. The ligands are expressed by the symbols in parentheses in Table 1. Triaminoguanidine nitrate was synthesized from aminoguanidine nitrate and hydrazine monohydrate, and the product was used after evaluating the purity by iodimetry.

The chemical formulas of the synthesized metal complexes are shown in Table 2 and are identified by the symbols in angle brackets in one table.

2.2 Apparatus and method

Differential thermal analysis and thermogravimetry were carried out using a Rigaku TAS-200 Thermal Analyzer. The sample container was an open alumina cell and the sample amount was 5 mg. The sam-

Table 2 Analytical Results

		C	H	N	M*
Zn(NN) ₃ (NO ₃) ₂ <ZnNN>	found	-	3.73	41.61	22.85
	calcd.	-	3.62	41.71	22.90
Zn(SB) ₃ (NO ₃) ₂ <ZnSB>	found	9.00	3.95	37.80	15.70
	calcd.	8.89	3.75	37.16	15.77
Zn(TAG) ₃ (NO ₃) ₂ <ZnTAG>	found	6.10	4.10	49.33	16.38
	calcd.	6.04	4.06	49.33	16.44
Cu(AG) ₃ (NO ₃) ₂ <CuAG>	found	7.23	3.73	41.61	18.90
	calcd.	7.15	3.62	41.71	18.93
Zn(UR) ₆ (NO ₃) ₂ <ZnUR>	found	12.90	4.41	35.13	11.78
	calcd.	13.09	4.39	35.60	11.89

M* : Metal

ple was heated to 800°C at a heating rate of 20°C/min. in air.

The qualitative analysis (TG-Mass measurement) of the evolved gases was carried out using Yokogawa mass spectrometer HP 5972 connected to a Rigaku TAS-300 Thermal analyzer. The sample container was an open alumina cell and the sample amount was 2mg. The sample was heated to 800°C at a heating rate of 20°C/min. in He.

3. Results and discussion

3.1 Synthesis of metal complex nitrates

Zn was chosen as the coordinated metal because of the coordination stability (natural order of stability), and Zn complex nitrates of various ligands were synthesized.

ZnNN was synthesized by mixing Zn nitrate hexahydrate with water and hydrazine monohydrate in a 1 to 3 of molecular ratio. In most cases, the metal elements in the first and third transition series form four- or six-coordinated complexes. However, the Zn complex coordinated with three moleculars of NN was obtained even on mixing with an extra NN (Zn nitrate : NN = 1 : 6).

ZnUR was synthesized based on the method of synthesizing the scandium complex perchlorate of urea. The coordination reaction progressed by heating to reflux at 40°C for a few hours after mixing Zn nitrate with methanol and urea. After cooling, the six-coordinated complex was obtained by concentration under reduced pressure.

On the other hand, SB could not be coordinated with metallic Zn by mixing Zn nitrate and SB chloride ; ZnSB was obtained from the Zn complex of ammine and SB chloride, as discussed below. The Zn complex of ammine was synthesized by the reaction of Zn nitrate and ammonia. Ammonia was added to the Zn nitrate with water little by little until a transparent solution was formed with the addition of ammonia, a white solid (the formation of ZnO) was first precipitated. The Zn complex of ammine was then obtained by the concentration of that solution under reduced pressure. The obtained ammine complex and SB chloride were mixed in a 1 to 3 molecular ratio and then refluxed at 70°C in a water bath for seven hours. Not SB nitrate but SB chloride was used because of high stability.

ZnTAG was also obtained from Zn complex nitrate of ammine and TAG nitrate by the same method as that for ZnSB synthesis.

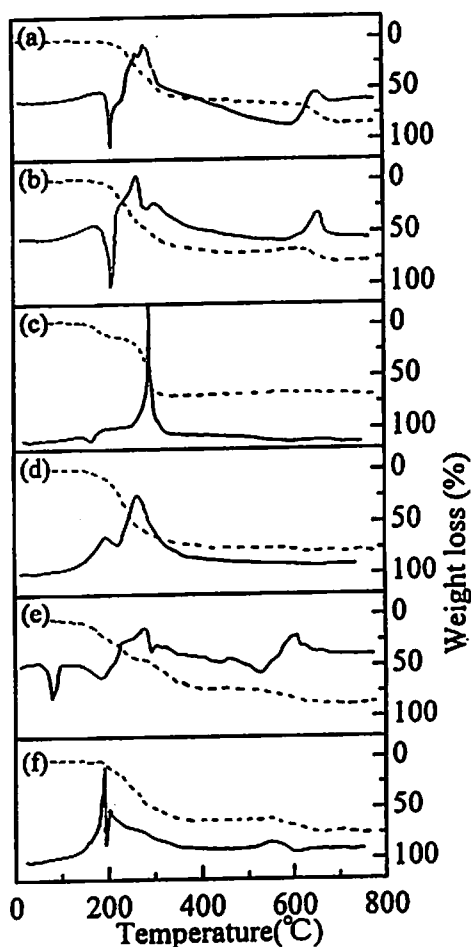
AG was coordinated with copper but could not be coordinated to a Zn. The Cu complex of AG was synthesized from the Cu complex of ammine and AG nitrate.

The obtained complexes were identified by elemental analysis and polarized light zeman atomic absorption spectrometry, because of insolubility in water. Table 2 shows the results of analysis of the obtained complexes.

3.2 Differential thermal analysis

Fig. 1 shows the results of the thermal analysis for five kinds of metal complexes. In this figure, the result for the Zn complex of CDH is also shown. The thermal behavior of ZnSB was apparently similar to that of the CDH complex, because the fundamental skeleton of both complexes is the same. The initial temperature of melting in the ZnSB was 20°C lower than that of the CDH complex.

For ZnNN, the exothermic decomposition with a sharp peak was confirmed after a small endothermic peak at 170°C. The residue after the first small endothermic peak at 170°C was recovered and analyzed by X-ray diffraction, because its peak might indicate the existence of an impurity. The diffraction pattern of the residue was not at all different from that of ZnNN. Furthermore, the absorbance of the nitrate ion was also confirmed in the IR spectrum of the residue. Consequently, in this stage, a part of the



(a) ZnCDH, (b) ZnSB, (c) ZnNN, (d) ZnTAG, (e) ZnUR, (f) CuAG

Fig. 1 DTA-TG curves for various metal complex nitrates

NN of the ligand might gradually decompose while retaining the form of the metal complex nitrate.

The ZnTAG and CuAG started to exothermally decompose at 170°C, and the decomposition reaction was complicated over a wide temperature range. For the ZnUR, the exothermic decomposition occurred above 120°C after melting at 90°C and gradually progressed to 650°C. The thermal stability of this complex was low.

In all complexes, the final decomposition residue was confirmed to be a bivalent metallic oxide from the final weight loss and x-ray diffraction.

3.3 Qualitative analysis of the evolved gas during the isothermal decomposition

Fig. 2 shows the change in the total ionic amount of the evolved gases during the decomposition at a heating rate of 20°C/min for the ZnTAG as a represen-

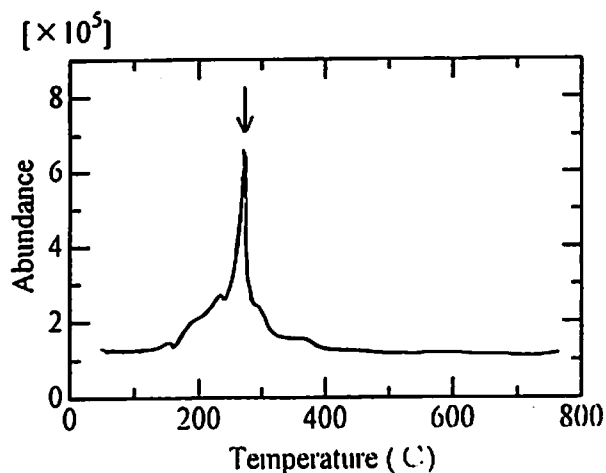


Fig. 2 The change in the total ionic amount of the evolved gases during the decomposition for the ZnTAG

tative example.

Gas started to evolve as soon as the weight of sample started to decrease due to the decomposition, and the gas evolution behavior was consistent with the thermal behavior seen in the DTA curve. Table 3 shows the fragment value obtained at the point in Fig. 2, in which the kind of the evolved gases was also presumed from the fragment value. Nitrogen gas is mainly evolved considering the structure. The kind of the gas scarcely changed during the reaction process, and Fig. 3 shows the change in the ionic amount of each fragment during the decomposition. At the initial stage of the reaction, nitrogen, hydrazine and ammonia gases were thought to evolve because of the detection of fragments 28, 32 and 17. In addition to these gases, carbon dioxide and nitrous oxide gases evolve above 200°C; fragments 44 and 30 were con-

Table 3 The fragment values for the evolved gases

m/e	components
17	NH ₃
18	H ₂ O
26	CN
28	N ₂ , CO
30	NO
32	N ₂ H ₄ , O ₂
44	N ₂ O, CO ₂

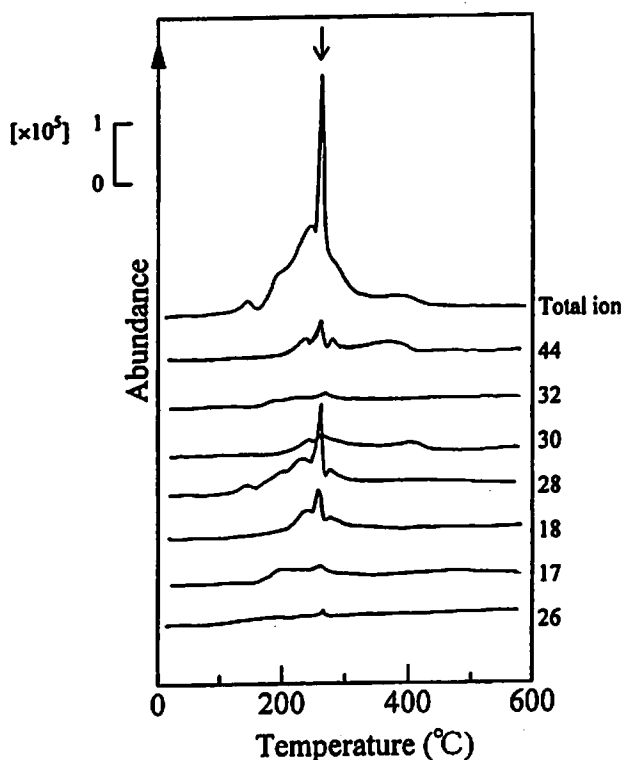


Fig. 3 The change in the ionic amount of each fragment during the decomposition for the ZnTAG

firmed, and the peak behavior of fragment 44 was consistent with that of fragments 28 and 30. At 400°C in the high temperature range, mainly nitrous oxide and nitrogen monoxide gases evolved based on the detection of fragments 44 and 30. Furthermore, hydrogen cyanide gas might evolve about 280°C based on the slight detection of fragment 27.

From the results of the measurement of TG-Mass for the five metal complexes, fragments 44, 32, 30, 28, 18 and 17 were fundamentally confirmed in all complexes. Fragment 26 detected slightly in ZnTAG was observed in CuAG also, which was thought to be due to the existence of the $-C=N-$ bond in both complexes. In ZnSB and ZnUR, fragment 43 was confirmed in addition to the above-mentioned six fragments. NH_2CO gas seems to be evolved due to the existence of the NH_2CO part in the structure of both complexes. Consequently, the evolution of not only carbon dioxide and nitrous oxide but also NH_2CO gas were assumed from the detection of fragment 44 in these complexes.

Furthermore, as one indication, the evolution ratio of each ionic amount to the total was calculated by the comparison of the peak height at the point in Fig.

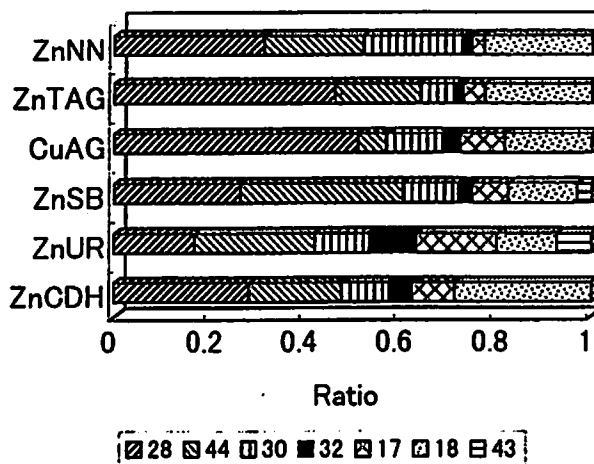


Fig. 4 The evolution ratio of the ionic amount of each fragment to the total

3 for the five complexes. Fig. 4 shows those results, in which the result obtained with the Zn complex nitrate of carbohydrazide is also shown for reference. In ZnTAG and CuAG, mainly nitrogen gas seemed to evolve during the decomposition considering the large evolution ratio of fragment 28. For ZnSB and ZnUR, an ionic amount of fragment 44 was considerably detected in comparison with the other complexes. The influence of NH_2CO evolution was thought to be large, as previously mentioned.

The quantitative analysis of the evolved gas will subsequently be investigated for these complexes.

4. Conclusion

Metal complex nitrates of hydrazine, semicarbazide, triaminoguanidine, aminoguanidine and urea were synthesized, and the gas evolution behavior was qualitatively investigated.

For the Zn complexes of hydrazine and triaminoguanidine and the Cu complex of aminoguanidine, fragment number 28 (N_2) was mainly confirmed during the decomposition at a heating rate of 20°C/min.

For the Zn complexes of semicarbazide and urea, mainly fragment number 44 (nitrous oxide or NH_2CO) was confirmed. In the case of the copper complex of aminoguanidine and the Zn complex of the triaminoguanidine, the evolution of cyan gas was suspected from the $-C=N-$ bonding in the structure.

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種々の金属錯体硝酸塩の熱的挙動(1) — 定性的なガス発生挙動 —

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新規のガス発生剤として期待される金属錯体硝酸塩を種々合成し、その定性的なガス発生挙動を検討した。合成したのは、ヒドラジン、セミカルバジド、トリアミノグアニジン及び尿素の亜鉛錯体とアミノグアニジンの銅錯体である。

昇温速度20℃/min. 下の熱分解において、ヒドラジン、トリアミノグアニジン及びアミノグアニジン(Cu)錯体はフラグメント28(N₂)が、セミカルバジド、尿素錯体はフラグメント44(N₂O及びNH₂CO)が主に確認された。アミノグアニジン(Cu)、トリアミノグアニジン錯体については、フラグメント26が確認され、構造中-C=N-があるため、シアンガスの発生が懸念される。

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