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# THERMAL BEHAVIOUR OF THE *N*-DONOR ADDUCTS OF METAL SACCHARINATES

## II. 1,10-phenanthroline saccharinato complexes of Co(II), Ni(II), Cu(II), Zn(II) and Pb(II)

*P. Naumov*[1*], *O. Grupče*[1], *V. Jordanovska*[1], *B. Boyanov*[2] *and G. Jovanovski*[1]

[1]Institute of Chemistry, Faculty of Science, ‘Sv. Kiril i Metodij’ University, P.O. Box 162, MK-91001 Skopje, Macedonia
[2] Faculty of Chemistry, Plovdiv University, Paisii Hilendarski, BG-4025 Plovdiv, Bulgaria

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## Abstract

Adducts of Co(II), Ni(II), Cu(II), Zn(II) and Pb(II) saccharinates with 1,10-phenathroline were synthesized and their thermoanalytical (TG, DTG and DTA) curves in the 20–1000°C temperature interval and static air atmosphere were recorded. The complexes are best represented as $M(C_{12}H_8N_2)_x(C_7H_4NO_3S)_2{\cdot}yH_2O$ ($x$=2, 2, 2, 2 and 1; $y$=1, 1, 2, 1 and 2 for $M$=Co, Ni, Cu, Zn and Pb, respectively). The decomposition of the compounds regularly started with dehydration, followed by loss of the phenanthroline ligand(s). The structures of the Cu and Pb complexes are notably different from other compounds. FTIR spectra of the title compounds in the region of the OH, CO and $SO_2$ stretching vibrations were also studied. The pronounced similarity of the spectra of Co, Ni and Zn adducts indicates possible isomorphism among them.

**Keywords:** *N*-donor adducts, 1,10-phenanthroline, saccharinates, thermal decomposition

## Introduction

The water-soluble salts (e.g., those of Na, K, $NH_4$ and Ca) of saccharin (1,2-benzisothiazol-3(2H)-one 1,1-dioxide) are widely used, mostly as artificial sweeteners and electroplating brighteners. However, the recent renewal of the discussions about the potential carcinogenic properties of saccharin has provoked considerable scientific attention for extensive structural studies of various metals saccharinates. In order to obtain additional information on the structure of these compounds, besides the X-ray diffraction and spectroscopic studies, much effort has also been made to investigate their thermal decomposition.

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* Author for correspondence: E-mail: spance@iunona.pmf.ukim.edu.mk

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Brief chronological outline of the existing literature data about the thermal properties of saccharinates will be presented in continuation of this text. Magri *et al.* [1] were first to describe the thermal decompositions of several saccharinates and pyridine saccharinates of Co(II), Ni(II), Cu(II) and Zn(II) [1, 2]. Additional data on the thermal behavior in the 303–623 K temperature interval of Ni(II), Cu(II), Zn(II) and Cd(II) pyridine saccharinates were reported later [3]. The decompositions of an oxo-vanadium(IV) complex described as a saccharin adduct [4] and some thermal data of $Cu(sac)_2 \cdot 6H_2O$[**] and of a mixed yttriumcopper ethanolate hydroxido complex were also presented [5]. The thermoanalytical curves of $Zn(py)_2(sac)_2$ were discussed in connection with its crystal structure [6]. Detailed reinvestigation of the thermal decompositions of the first transition row saccharinates of type $[M(H_2O)_4(sac)_2] \cdot 2H_2O$ (*M*=Mn, Fe, Co, Ni, Cu, Zn) together with a systematic kinetic analysis of the dehydration process was undertaken by Içbudak *et al.* [7]. These authors also reported the thermal properties of the mixed hydrazine and ethylenediamine saccharinates of Co(II), Ni(II) and Cu(II) [8]. We have recently presented data on the thermal decompositions of the pyridine saccharinates $[M(H_2O)_4(py)_2](sac)_2 \cdot 4H_2O$ (*M*=Co and Ni) and $[Cu(sac)_2(H_2O)(py)_2]$ [9], and of 2,2'-bipyridine saccharinates of Co(II), Ni(II), Cu(II), Zn(II) and Pb(II) [10]. Very recently we have also investigated the thermal decomposition of all alkali saccharinates (except for the Li salt) [11].

In the present paper, the results of the study of the thermal decomposition of Co(II), Ni(II), Cu(II), Zn(II) and Pb(II) complexes with saccharin and 1,10-phenanthroline are reported. The decomposition pathways of the complexes are discussed in connection with the thermal data for the corresponding pyridine and 2,2'-bipyridine complexes, the X-ray diffraction data for the phenanthroline Cu(II) complex [12] and those obtained by the FTIR spectroscopy. Certain structural characteristics of the complexes are predicted.

### *Structural data about 1,10-phenanthroline saccharinato complexes*

From mixed phenanthroline-saccharinato complexes of the cations investigated in this study only the crystal structure of a Cu(II) compound, characterized as $[Cu(phen)_2(sac)](sac) \cdot 2H_2O$ was determined [12]. The crystals are triclinic ($P\bar{1}$, No. 2), with two formula units per unit cell. The structure consists of $[Cu(phen)_2(sac)]^+$ cations and uncoordinated saccharinato anions and water molecules. The Cu atom is trigonal-bipyramidally coordinated by one saccharinato ligand and two bidentate phenanthroline molecules.

The structure of Mn(II) phenanthroline saccharinato complex, $[Mn(phen)_2(sac)_2(H_2O)_2] \cdot H_2O$ was reported as well [13]. The compound crystallizes in the triclinic sytem ($P\bar{1}$, No. 2) with two formula units per unit cell. Its crystal structure is composed of $Mn(phen)_2(H_2O)_2^{2+}$ moieties, saccharinato ions and uncoordinated water molecules. The saccharinato ions are not included in the first coordination sphere of the cation, but interact with the metal through hydrogen bonds with the coordinated water molecules. The structure of another, monohydrate complex, $[Mn(phen)_2(sac)(H_2O)](sac)$, has been reported very recently [14].

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[**] In the text sac stands for saccharinato ion/ligand, py – denotes pyridine, phen – 1,10 phenanthroline

## Experimental

The complexes were prepared from the respective metal(II) acetates or carbonates, 1,10-phenanthroline and saccharin mixed in stoichiometric ratio.

The DTA, DTG and TG studies were carried out in Pt crucibles and static air atmosphere on a Q Derivatograph MOM, Hungary, in the temperature range from room temperature to approximately 1000°C. The mass of the samples was 50 mg, $\beta$=10°C min$^{-1}$.

The FTIR spectra in the 4000–400 cm$^{-1}$ frequency range were recorded from KBr pellets with System 2000 interferometer (Perkin Elmer). Graseby Specac P/N 21525 variable-temperature cell with KBr windows was used to record the spectra at the boiling temperature of liquid nitrogen (LNT).

## Results and discussion

The thermoanalytical curves of the studied complexes are presented in Figs 1–5. The corresponding IR and thermal decomposition data are summarized in Tables 1 and 2, respectively. According to the results from the TG analysis, the complexes are best represented as $M(C_{12}H_8N_2)_x(C_7H_4NO_3S)_2 \cdot yH_2O$ ($x$=2, 2, 2, 2 and 1; $y$=1, 1, 2, 1, 2 for $M$=Co, Ni, Cu, Zn and Pb, respectively).

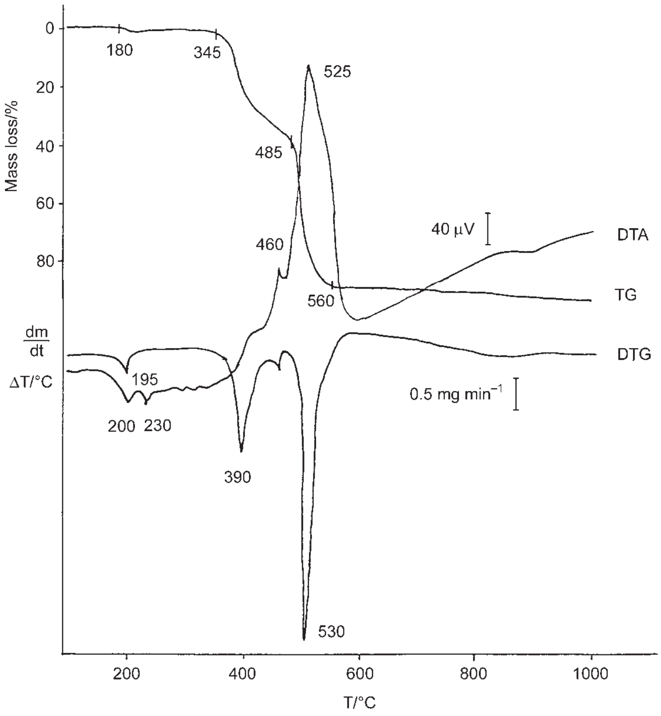

**Fig. 1** TG, DTG and DTA curves of $Co(phen)_2(sac)_2 \cdot H_2O$

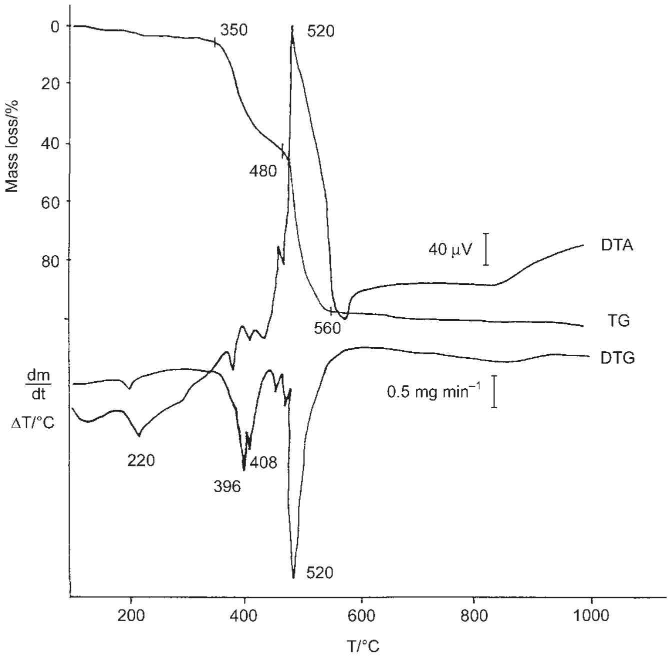

Fig. 2 TG, DTG and DTA curves of $Ni(phen)_2(sac)_2{\cdot}H_2O$

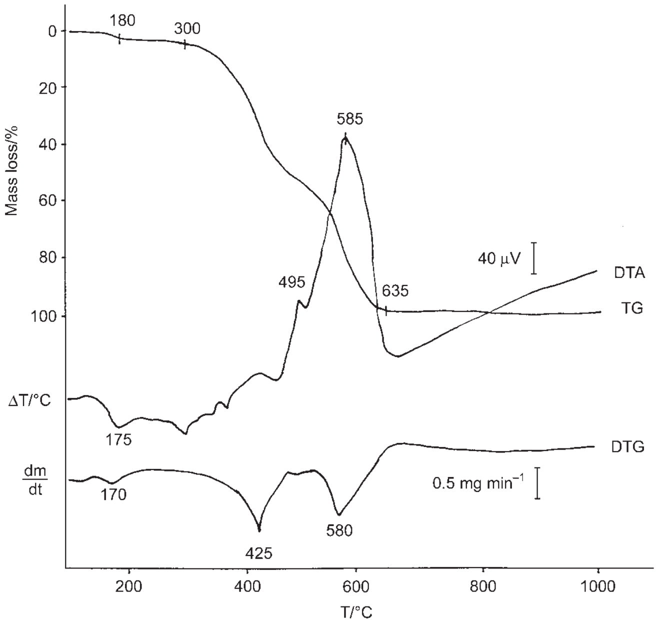

Fig. 3 TG, DTG and DTA curves of $Zn(phen)_2(sac)_2{\cdot}H_2O$

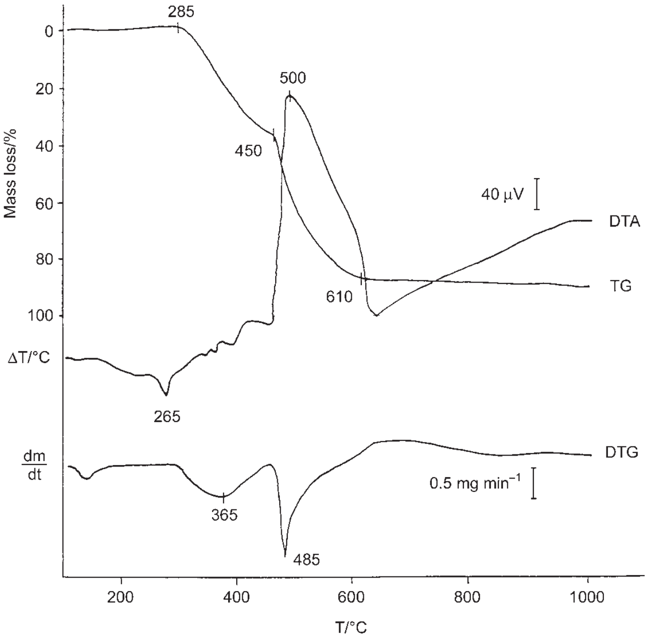

**Fig. 4** TG, DTG and DTA curves of $Cu(phen)_2(sac)$

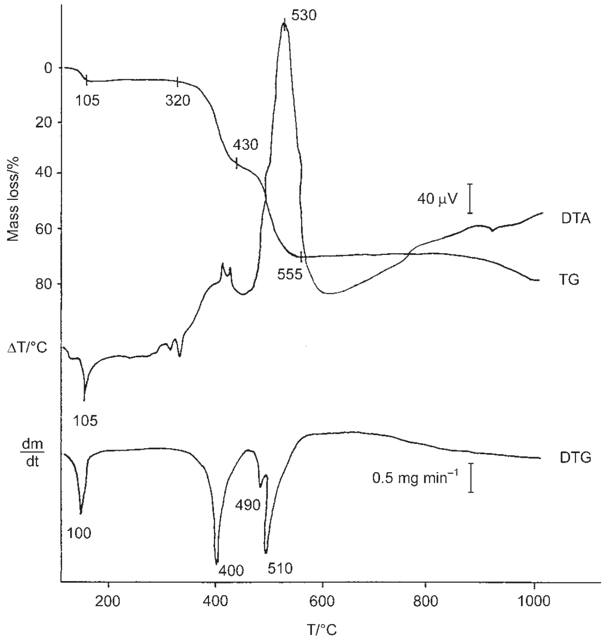

**Fig. 5** TG, DTG and DTA curves of $Pb(phen)(sac)_2{\cdot}2H_2O$

**Table 1** LNT FTIR data for the 1,10-phenanthroline saccharinates of Co(II), Ni(II), Cu(II), Zn(II) and Pb(II)

| Compound | Vibrational frequency/cm$^{-1}$ | | | |
|---|---|---|---|---|
| | $\nu$(OH) | $\nu$(CO) | $\nu_{as}$($SO_2$) | $\nu_s$($SO_2$) |
| Co | 3310–3066 | 1646<br>1623 | 1302<br>1240 | 1157<br>1148 |
| Ni | 3353–3066 | 1645<br>1624 | 1302<br>1241 | 1158<br>1137 |
| Cu | 3606–3381 | 1665 | 1268<br>1259 | 1152<br>1141 |
| Zn | 3337–3147 | 1646<br>1627 | 1304<br>1241 | 1151<br>1136 |
| Pb | 3461–3077 | 1613<br>1601 | 1281<br>1270 | 1156<br>1143 |

**Table 2** Thermal decomposition data for 1,10-phenanthroline saccharinates of Co (II), Ni (II), Cu(II), Zn(II) and Pb(II)

| | Temperature range/°C | DTA$_{max}$/ °C$^a$ | Removed species | Mass loss/% | | Observed total mass loss/% |
|---|---|---|---|---|---|---|
| | | | | observed | calculated | |
| $Co(phen)_2(sac)_2 \cdot H_2O$ | | | | | | |
| 1 | 170–230 | 200(–),230(–)m | $H_2O$ | 2 | 2.2 | |
| 2 | 345–485 | 460(+) | phen,2$SO_2$ | 38 | 37.5 | |
| 3 | 485–560 | 525(+) | undefined | | | 90 |
| $Ni(phen)_2(sac)_2 \cdot H_2O$ | | | | | | |
| 1 | 180–230 | 220(–)m | $H_2O$ | 2 | 2.2 | |
| 2 | 350–465 | c(–) | phen,2$SO_2$ | 38 | 38.5 | |
| 3 | 465–560 | 520(+) | undefined | | | 100 |
| $Zn(phen)_2(sac)_2 \cdot H_2O$ | | | | | | |
| 1 | 160–220 | 300(–)m | $H_2O$ | 2 | 2.29 | |
| 2 | 300–460 | c(–) | 2phen,$SO_2$ | 52 | 52.52 | |
| 3 | 460–635 | 495(+),585(+) | undefined | | | 100 |
| $Cu(phen)_2(sac)_2$ | | | | | | |
| 1 | 285–450 | c(–),265(–)m | phen,2$SO_2$ | 38 | 38.06 | |
| 2 | 450–610 | 500(+) | undefined | | | 92 |
| $Pb(phen)(sac)_2 \cdot 2H_2O$ | | | | | | |
| 1 | 80–105 | 105(–) | 2$H_2O$ | 5 | 4.58 | |
| 2 | 320–460 | c(+) | phen,$SO_2$ | 32 | 31.16 | |
| 3 | 460–555 | 530(+) | undefined | | | 71 |

[a] Symbols denote: (+) – exothermic, (–) – endothermic, c – complex, m – melting

## *Infrared spectra*

The characteristic OH, CO and $SO_2$ stretching frequencies of the complexes are summarized in Table 1. All complexes are solid hydrates, as it follows from the presence of the characteristic ν(OH) bands in their FTIR spectra. The pronounced spectral similarity of the Co, Ni and Zn adducts at LNT indicates possible isomorphism among these compounds. The frequencies of the ν(CO) bands as well as those due to the $SO_2$ stretching (antisymmetric and symmetric) modes of all adducts are lower than the respective modes of saccharin. This is caused by electronic differences between the neutral saccharinato molecule and the corresponding nitranion [15–17], rather than by $O_{SO_2}$ – or $O_{CO}$-coordination, as it was previously presumed.

## *Thermal decomposition*

In general, the decomposition pathways of the 1,10-phenanthroline adducts resemble those of the respective 2,2'-bipyridine complexes [10], i. e. the Co, Ni and Zn compounds decompose in a similar manner, and, at the same time, appreciably different from the Cu and Pb compounds. However, certain differences are also present.

### $M(phen)_2(sac)_2\cdot H_2O$ (*M*=Co, Ni and Zn)

Thermal decompositions of the Co, Ni and Zn adducts (Figs 1–3) proceed in three stages. The first stage is related to dehydration. According to the DTG peaks corresponding to this process, the least stable is the Zn complex (170°C), while the Co (195°C) and Ni (208°C) complexes are more stable, which is consistent with the data obtained from the IR study. The DTA peaks at 230 (Co), 220 (Ni) and 300°C (Zn) that are not associated with significant TG effects are in connection with subsequent melting of the anhydrous complexes.

The temperature on the onset of the second decomposition stage of the Zn complex (Fig. 3) is also the lowest one of all three compounds and not well resolved from the dehydration stage. Single DTG peak (at 425°C for the Zn adduct, Fig. 3) or pairs of DTG peaks (at 390 and 406°C for the Co adduct, Fig. 1, and at 396 and 408°C for the Ni adduct, Fig. 2) correspond to this process. During this stage, the Co and Ni compounds release one phenanthroline and two $SO_2$ molecules, while in the case of Zn complex two phenanthroline and one $SO_2$ molecules per formula unit are released. Such a behaviour implies that (at least with respect to the phenanthroline ligands) the Co and Ni compounds are structurally similar, but different from the Zn complex.

Similarly to the bipyridine saccharinates [10], the third stage is associated with a strong exothermic redox process (exothermic DTA peaks at 525, 520 and 585°C with corresponding DTG peaks at almost equal temperatures in case of Co, Ni and Zn complexes, respectively). During this stage, the remaining organic part is abruptly burnt in all compounds. The mass loss of nearly 100% obtained at the end of this stage in case of the Ni and Zn complexes (Figs 2 and 3, TG curves) suggests that the crucible has been emptied during the preceding vigorous reaction. On the other hand, the continuous mass loss of about 4% observed for the residue from the Co complex

(Fig. 1, TG curve), implies that the remaining carbon is slowly oxidized afterwards. According to the overall mass loss (Table 2), the thermal decomposition of Co phenanthroline saccharinate results in carbonaceous product, instead of the expected formation of the metal oxide in air atmosphere. Such a behavior has been already found in other metal-organic compounds of Co [18]. This could be explained by the existence of strong reducing environment in static air atmosphere containing abundant carbon after burning of the organic residue.

## Thermal decomposition of $Cu(phen)_2(sac)_2$

The thermal decomposition of the Cu complex (Fig. 4) proceeds in two stages. Interestingly, except for the broad peak on the DTG curve, no defined peak was found to correspond to dehydration in this compound. On the other hand, X-ray diffraction [12] and our spectroscopic investigations (Table 1, [19]) have characterized this compound as dihydrate. One of the explanations for this discrepancy can be very low temperature of the dehydration, just above room temperature i.e. at the onset of heating. At least three reasons can be mentioned here for such presumptions:

a. Broad peak is present on the DTG curve just above the room temperature that may be due to immediate loss of the water molecules. It is in line with our previous experience that the copper complexes are the most unstable within a given series of adducts,

b. The water molecules in the complex are not coordinated to the metal and thus they might be loosely bound in the lattice, and

c. Large heating rate (10°C $min^{-1}$) used in the study. The temperature of further decomposition of the dehydrated complex is somewhat lower than the other adducts in this study. The onset of the first stage is at 285°C, when, similarly to the Ni and Co complexes, one molecule of phenanthroline and two molecules $SO_2$ are released. The endothermic peak at 265°C is not associated with any observable mass loss and can be attributed to melting of the residue. The ‘waved’ shape of the DTA curve characteristic of the release of the *N*-donor ligand is observed up to 450°C.

The second stage is associated with the release of the second phenanthroline molecule and decomposition of the remaining organic part of the saccharinato ligands. The release of the phenanthroline molecules during different stages might indicate certain structural differences between these ligands in the complex [12]. A strong DTA peak (500°C), along with a DTG maximum (485°C) characterizes the subsequent redox process. Considering the total mass loss values and the chemical behavior of the final product (Table 2), it could be supposed that carbonaceous elementary copper is obtained, similarly to what was found for the respective bipyridine complex [10, 18].

## Thermal decomposition of $Pb(phen)(sac)_2 \cdot 2H_2O$

Proceeding in three stages, the thermal decomposition of the Pb adduct reminds of those of the Co, Ni and Zn complexes. Nevertheless, the decomposition stages in case of the Pb complex are apparently resolved better (Fig. 5). During the first stage the compound is dehydrated. The two water molecules leave the complex simultaneously, which is illustrated by the single DTG and DTA maxima at 100 and 105°C, respectively.

The second stage starts above 320°C with simultaneous release of the phenanthroline ligand and one $SO_2$ molecule (single DTG maximum at 400°C). During the third stage the rest of the complex is decomposed. This strongly exothermic redox process is accompanied by a DTA maximum at 530 and a shoulder at approximately 490°C. The process is probably complex, as it can be inspected from the presence of two DTG maxima (490 and 510°C). The experimentally observed mass loss is greater than expected for lead(II) oxide. It is probable, therefore, that there was a leak from the crucible during the vigorous exothermic redox reaction. Analogous to the bipyridine adduct of Pb(II) saccharinate [10], it can be supposed that the final product might be carbonaceous lead [18].

## Conclusions

On the basis of the thermal data, the empirical formula of the complexes can be represented as $M(C_{12}H_8N_2)_x(C_7H_4NO_3S)_2{\cdot}yH_2O$ ($x$=2, 2, 2 and 1; $y$=1, 1, 1 and 2 for $M$=Co, Ni, Zn and Pb, respectively). The thermoanalytical curves of the Cu(II) complex recorded in this study, could not prove the existence of the water molecules in the structure. Except for this complex, the thermal decomposition of the complexes proceeds in three stages, the first one being the dehydration process. One or two (for the Zn complex) phenathroline ligand(s) and $SO_2$ are released during the second stage, while the organic residue burns during the third, exothermic stage.

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