THREE NEW DINUCLEAR SILVER(I) COMPLEXES DERIVED FROM PYRAZOLYL TYPE LIGANDS
Crystal structure and thermal decomposition

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Three NNN type ligands derived from 2,6-dichloropyridine, pyrazol and 3,5-dimethylpyrazole and their silver complexes were prepared in methanol media. The complex structures were characterized using IR spectroscopy, X-ray diffraction and elemental analysis. X-ray studies showed the complexes to be dimeric in structure. The two nitrogen atoms of the ligand coordinated the first Ag(I) ion whereas the second Ag(I) ion was coordinated by the third nitrogen donor. The nitrate structure was not ionic in a done of its oxygen atoms coordinated an Ag(I) ion. The Ag(I) ion was seen to be situated in a deformed tetrahedral coordination sphere. Thermogravimetric studies showed the complexes to decompose similar to explosive material. The decomposition temperature was observed to increase with increasing hydrogen atoms in the structure.

Keywords: DTA, pyrazolyl, silver(I) complex, TG

Introduction

Bis-2,6-(Pyrazol-1-yl) pyridine (pp) and *bis*-2,6-(3,5-dimethylpyrazol-1-yl) pyridine are two terpyridine type ligands being used since 1990 [1]. Due to their inexpensive and easy synthesis method they are frequently seen in coordination chemistry literature. Their planar structure and geometric position of the three nitrogen atoms ensure them to be strong ligands in both acidic and alkaline media. Studies dealing with transition metal complexes of these ligands have been reported in literature [2–8].

In recent years, many studies dealing with silver(I) complexes in N_4 [9–13], N_3 [14, 15], N_2 [16], N_2O_2 [17] and N_3O [18] coordination spheres have been reported.

Ag(I) complexes coordinated by nitrogen donors and nitrate ions have also been reported ecently [17–18]. The nitrate ion is seen to participate in the coordination structure in both complexes whereas formation of a μ-bridge, leading to a dinuclear complex structure is observed with one of the ligands. In another study with a similar NNN type ligand, silver(I) is coordinated by two of the nitrogen donor atoms, whereas the third nitrogen atom coordinates another silver(I) ion [19, 20].

In this paper we describe the synthesis and TG-DSC analysis of some silver(I) complexes with NNN type pyrazolyl ligands. We have not come across any TG-DSC studies related to Ag(I) ion complexes. A schematic representation of the ligands and complex is given in Fig. 1. Appropriate crystals for only one of the complex structure was possible ([AgdmppNO$_3$]$_2$). Thus molecular model for only this complex is given.
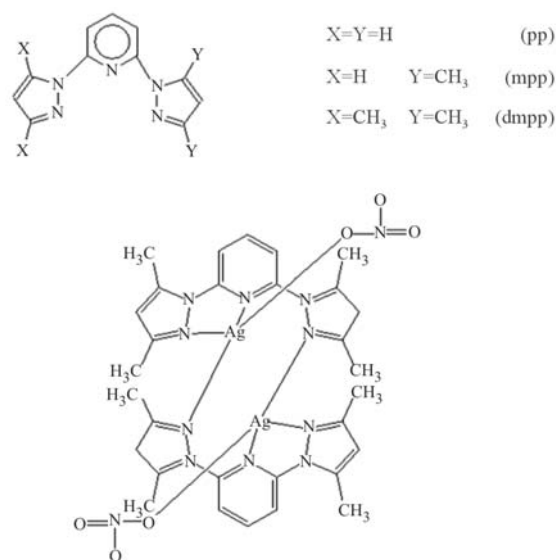

Fig. 1 Schematic representation of the ligands and [AgdmppNO$_3$]$_2$ complex

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Experimental

Preparation of materials

The ligands pp, mpp and dmpp were prepared according to literature [1]. Elemental analysis and important IR data are given in Table 1.

Preparation of pp

6.8 g of pyrazol was dissolved in 100 mL of diethylene glycol dimethyl ether (diglym) at 50°C. 2.4 g (0.104 mole) of metallic Na was added in small fragments and the solution was stirred for 2 h resulting in the formation of sodium pyrazolate. The unreacted sodium fragments were separated and 7.4 g (0.05 mole) of 2,6-dichloropyridine was added to the solution. The solution was stirred for two days in a temperature range of 110–130°C. The resulting mixture was poured into 600 mL of water-ice mixture and the resulting precipitate was filtered and dried under atmosphere conditions. The dry precipitate was crystallized in a MeOH:H_2O (1:2) mixture.

Preparation of mpp

6.8 g (0.1 mole) of pyrazol was dissolved in 100 mL diglym at 50°C. 2.4 g (0.104 mole) of metallic Na was added in small fragment and the solution was stirred for 2 h resulting in the formation of sodium pyrazolate. The unreacted Na pieces were separated and 14.8 g (0.1 mole) of 2,6-dichloropyridine was added to the solution. The mixture was stirred for two days at 60°C on a water bath. The mixture was then poured onto 600 mL of an ice-water mixture and the resulting precipitate filtered and dried. The precipitate was identified as 2-pyrazol-1-yl-6-chloro pyridine. Yield: 65%.

An equimolar amount of 3,5-dimethylpyrazole was dissolved in diglym and reacted with 2.4 g of metallic sodium. 2-pyrazol-1-yl-6-chloro pyridine was added to this solution and stirred for two days in the temperature range of 110–130°C. The mixture was then poured onto 600 mL of water-ice mixture and the resulting precipitate was filtered and dried. The dry crystals were recrystallized in a MeOH:H_2O (1:1) mixture.

Preparation of dmpp

9.6 g (0.1 mole) 3,5-dimethyl pyrazole was reacted with 2.4 g (0.104 mole) of metallic sodium for 2 h in 100 mL of diglym. The unreacted sodium particles were separated and the 7.4 g (0.05 mole) of 2,6-dichloropyridine was added to the solution and stirred for 2 days at 110–130°C. This mixture was poured over 600 mL of iced water and the precipitate was filtered and recrystallized in a MeOH:H_2O (1:1) mixture.

Preparation of complexes

All three complexes were prepared according to the same procedure. 0.001 moles of pp, mpp or dmpp was dissolved in 50 mL of MeOH. To this solution was added the solution of 0.17 g (0.001 mole) of $AgNO_3$ in 20 mL MeOH:H_2O (3:1) mixture. The resulting solution was filtered using a Whatman 42 filter paper. The solution was left to stand for two days and the crystalline precipitate was filtered and dried at 80°C. Elemental analysis results and important IR data are given in Table 1.

Methods

Element analysis was performed using a Leco 932 CHNS instrument. Ag analysis was done titrimetrically according to the Volhardt method. The Ag complex was first boiled in HNO_3 and the Volhardt method was then employed.

IR spectrums were obtained with a Mattson 1000 FTIR using KBr disks. Thermal analysis was performed using Shimadzu DTG-60 and DSC-60 instruments.

TG curves were obtained between 30–750°C with a heating rate of 10°C min^{-1} and N_2 flow of 100 mL min^{-1}. DSC curves were obtained between 30–400°C with a heating rate of 10°C min^{-1} and N_2 flow of 30 mL min^{-1}.

Intensity data were collected at room temperature using an Enraf-Nonius CAD 4 diffractometer [21] with MoK_α radiation using $\omega/2\theta$ scan mode. Cell parameters were determined from least squares analysis using 25 centred reflections in the range of $2.67 \leq \theta \leq 26.28$. Three standard reflections for every 120 min during data collection showed no significant intensity variations. The structure was solved by direct methods using the solution program SHELXS97 [22] in the WinGX package [23] and refined using SHELXL97. All non-hydrogen atoms were refined, first with isotropic and then anisotropic thermal displacement parameters, by full matrix least square techniques. All the hydrogen atoms were placed geometrically and refined as riding with $U_{iso}(H)=1.2U_{eq}(C)$.

Results and discussion

A PLATON drawing [24] of the molecule, [AgdmppNO$_3$]$_2$, with 50% probability displacement thermal ellipsoids and atomic numbering scheme is shown in Fig. 2 and intermolecular agostic interaction is shown in Fig. 3. The X-ray diffraction data collection and crystal data are given in Table 2, where as coordinate bond lengths and angles of the complex are given in Table 3. Table 4 represents the intermolecular agostic hydrogen bonding geometry.

Table 1 Element analysis results and important IR data

Ligands and complexes	Yield/%	m.p./°C	Element analysis								Important IR data/cm^{-1}						
			expected/%				found/%				γ_{C-H} aromatic	γ_{C-H} aliphatic	$\gamma_{C=C}$ ring	$\gamma_{C=N}$ ring	δ_{CH_3}	$\gamma_{N=O}$	δ_{C-H} aromatic
			C	H	N	Ag	C	H	N	Ag							
pp $C_{11}H_9N_5$	76	134	62.57	4.29	33.16	–	63.02	4.34	34.83	–	3105 3080	2978 2920	1591	1562	–	–	797
mpp $C_{13}H_{13}N_5$	57	94–97	65.26	5.47	29.60	–	65.33	4.96	30.12	–	3113 3071	2974 2849	1591	1571	1454	–	804
dmpp $C_{15}H_{17}N_5$	57	106	67.40	6.41	26.19	–	66.92	6.56	27.28	–	3109 3084	2978 2857	1592	1562	1448	–	801
[AgppNO$_3$]$_2$	72	–	34.67	2.38	22.04	28.31	34.91	3.12	20.96	28.42	3112 3074	–	1597	1574	–	1379	793
[AgmppNO$_3$]$_2$	60	–	38.16	3.20	20.53	26.37	37.73	3.86	20.12	25.90	3108 3078	2976 2864	1595	1576	1452	–	796
[AgdmppNO$_3$]$_2$	62	–	41.21	3.91	19.21	24.67	41.72	4.22	18.17	24.38	3122 3081	2974 2852	1594	1584	1449	1340	791

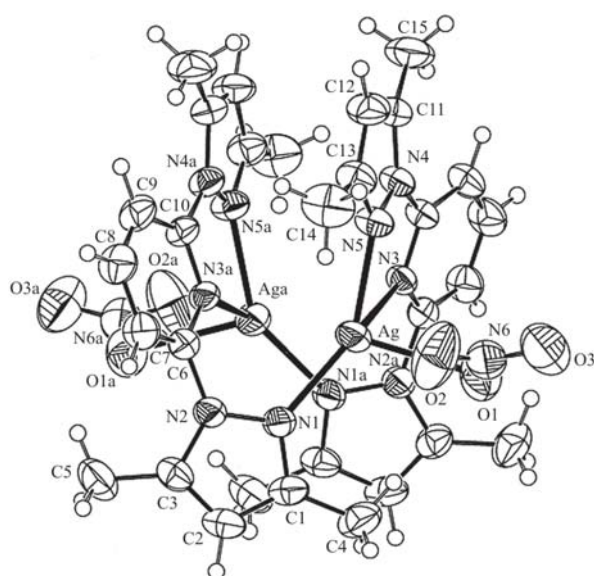**Fig. 2** PLATON drawing of the [AgdmppNO₃]₂ complex
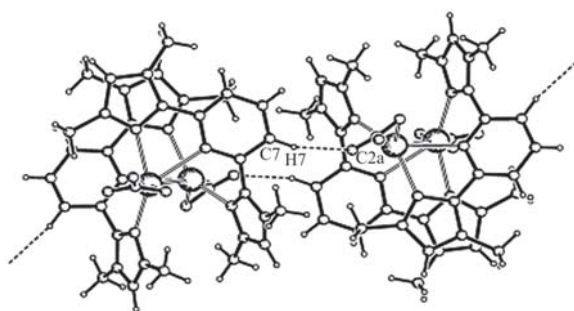
Fig. 3 PLATON drawing of intermolecular hydrogen bonds
(agostic interactions)

Table 2 Crystal and experimental data of AgdmppNO₃ complex

Chemical formula	$C_{15}H_{17}AgN_6O_3$
Formula mass	437.22
Temperature/K	293(2)
Wavelength/Å	0.71073
Crystal system, space group	monoclinic, C2/c
Unit cell dimensions/Å, degree	
A	19.0304(12)
B	12.2898(11)
C	16.6980(13)
β	119.329(3)
Volume/Å³	3404.7(5)
Z	8
Calculated density/g cm⁻³	1.706
Absorption coefficient/mm⁻¹	1.212
F(000)	1760
Crystal size/mm	0.30×0.25×0.20
θ_{max}/degree	52.56
Index range	−20≤h≤23, −15≤k≤0, −20≤l≤0
Number of reflections used	2356 (I≥2σ(I))
Number of parameters	227
R_{int}	0.016
R	0.038
R_w	0.104
Goodness of fit	0.98
$\Delta\rho_{min}$, $\Delta\rho_{max}$/e Å⁻³	−0.445, 0.971 Q1 (0.95 Å from Ag) Q2 (1.00 Å from Ag)

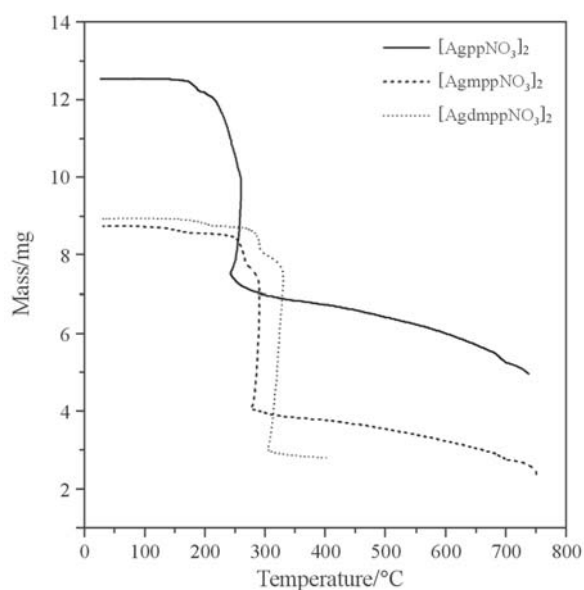The dimeric nature of the molecule can be observed from Fig. 4. Similar results with resembling ligands have been reported in literature [19]. The Ag(I) ion is within the tetrahedral N₃O coordination sphere. While two of the three nitrogen donors and the nitrate oxygen coordinates one Ag(I) ion, the third nitrogen coordinates another Ag(I) ion resulting in the formation of a bidentate complex. Tetrahedral coordination is the most frequently observed structure for Ag(I) [25]. But the tetrahedral structure here is extremely deformed, as the three donor atoms of the ligand, do not possess the geometry to coordinate three corners of a tetrahedron. The angles around Ag for the N₃AgN₅, N₃AgO₁, N₁AgN₃, N₁AgO₁ and N₁AgN₅ are 67.46(11)°, 84.89(13)°, 133.35(12)°, 112.15(13)° and 145.21(13)° respectively. Although by looking at these angles it is diffucult to quote a tetrahedral coordination similar results are given in literature. Table 5 shows the smallest and largest angles for four different silver complexes.

The degree of distortion for tetrahedral coordination is defined a θ as suggested by Dobson *et al.* [26]. θ

Fig. 4 TG curves of the complexes

Table 3 Selected bond lengths (Å) and angles (°) of the Ag(I) complex

Ag		Aga	3.1574(7)
Ag		O1	2.592(4)
Ag		N1	2.206(3)
Ag		N3a	2.530(3)
Ag		N5a	2.274(3)
N1		N2	1.367(4)
N4		N5	1.353(4)
N6		O1	1.260(5)
N6		O2	1.211(6)
N6		O3	1.237(6)
N1	Ag	N5a	145.27(11)
N1	Ag	N3a	133.29(11)
N5a	Ag	N3a	67.52(10)
N1	Ag	O1	112.12(13)
N5	Ag	O1a	95.37(13)
N3	Ag	O1a	84.76(12)
N1	Ag	Aga	78.40(9)
N5	Ag	Aga	95.92(8)
N3	Ag	Aga	62.30(7)
O1	Ag	Aga	137.33(10)

Symmetry code : (a) $1-x,y,1/2-z$

Table 4 Hydrogen bonding geometry/Å, degree

D–H…A	D–H	H…A	D–A	D–H…A
C7–H7…O2a	0.95	2.55	3.363(6)	143

Symmetry codes: (i) $1/2-x,1/2-y,-z$

Table 5 Smallest and largest angles for four different silver complexes

Coordination sphere around Ag(I)	Smallest and largest angles	Reference
N_2O_2	68.5–145.24	17
N_4	72.9–152.9	20
N_3O	92.7–128.6	18
N_2O_2	88.5–120.71	14
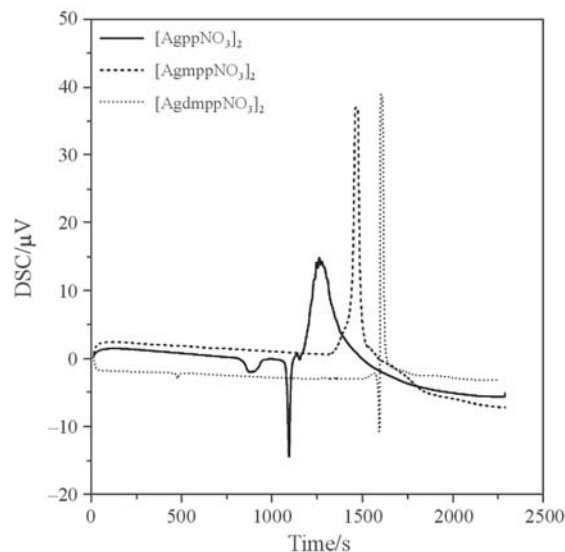
Fig. 5 DSC curves of the complexes

is an angle value expressing deviation from the x, y and z axis. These values are given 90° in an ideal tetrahedron. Calculation of these values according to literature [27] gives Q_x=119.27°, Q_y=96.52° and Q_z=90.42°. These angles prove the tetrahedron to be distorted.

A recent study dealing with pyrazolyl complexes has been reported in literature [27]. In this study the thermal decomposition of nickel (II) pyrazolyl thiocyanate complexes are given. In our case, the situation is quite different. It is stated that in these types of complexes decomposition of pyrazoly is followed by the decomposition of thiocyanate. Whereasa in the present manuscript an explosive reaction takes place.

Figures 4 and 5 show the TG and DSC results of [AgppNO₃]₂, [AgmppNO₃]₂ and [AgdmppNO₃]₂. Each curve was repeated 5 times. The mass loss for each complex is as follows; 48.62±1.12% between 246.7–255.1°C for [AgppNO₃]₂, 57.29±0.76% between 282.8–284.5°C for [AgmppNO₃]₂ and 66.54±1.33% between 299–315°C for [AgdmppNO₃]₂. The residue following analysis was 51.38, 42.71 and 33.46%, respectively. The heat of decomposition was found as 576.92±54.36 J g⁻¹ (439.68 kJ mol⁻¹), 221.83±23.54 J g⁻¹ (180.58 kJ mol⁻¹) and 106.50±16.80 J g⁻¹ (93.12 kJ mol⁻¹) for [AgppNO₃]₂, [AgmppNO₃]₂ and [AgdmppNO₃]₂ respectively (Fig. 5).

Examination of the TG results show the complexes in question to decompose at a certain temperature with an inner reaction. The mass loss for each [AgppNO₃]₂, [AgmppNO₃]₂ and [AgdmppNO₃]₂ complexes are 48.62±1.12, 57.29±0.76 and 66.54±1.33%,

$$\Omega = \frac{[\text{oxygen number in the molecule} - \text{required oxygen number}]\cdot 16}{\text{molecular mass}}\cdot 100$$

$$\text{required oxygen number} = \left[\begin{array}{c}\text{oxygen number required to convert all carbon atoms to } CO_2\end{array} + \begin{array}{c}\text{oxygen number required to convert all H atom to } H_2O\end{array} + \begin{array}{c}\text{oxygen number required to convert of metal atoms to their oxide form}\end{array}\right]$$
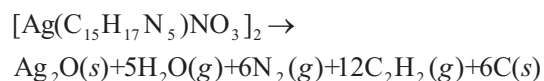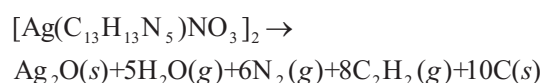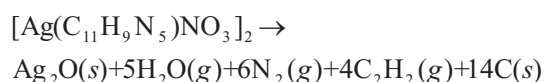
Equation (1)

respectively. The residue left in the alumina pan, on the other hand,are 51.38, 42.71 and 33.46%, respectively. Examination of the mass loss and residue is proof of an explosive inner reaction observed for explosive material. The oxygen balance parameter (Ω) given for explosive material is a well known fact [27, 28]. This value is utilized in the evaluation of explosive inner reaction and is calculated according to Eq. (1).

If Ω is more negative than –40% then the following rules apply.

• All metal atoms form metal oxides.
• $H_2O(g)$ is formed with the remaining oxygens.
• $CO_2(g)$ is formed with the remaining oxygens.
• All nitrogen atoms reconverted to $N_2(g)$.
• The remaining C and H atoms a reconverted to $CH_4(g)$, $C_2H_4(g)$ and $C_2H_2(g)$ accordingly.
• If any C residue is left it remains as solid C.

In accordance with these rules Ω is calculated as –54.589, –66.49 and –76.86% for [AgppNO$_3$]$_2$, [AgmppNO$_3$]$_2$ and [AgdmppNO$_3$]$_2$, respectively. All values are more negative than –40%. Accordingly the following thermal inner reaction can be written.

$$[Ag(C_{11}H_9N_5)NO_3]_2 \rightarrow$$
$$Ag_2O(s)+5H_2O(g)+6N_2(g)+4C_2H_2(g)+14C(s)$$

$$[Ag(C_{13}H_{13}N_5)NO_3]_2 \rightarrow$$
$$Ag_2O(s)+5H_2O(g)+6N_2(g)+8C_2H_2(g)+10C(s)$$

$$[Ag(C_{15}H_{17}N_5)NO_3]_2 \rightarrow$$
$$Ag_2O(s)+5H_2O(g)+6N_2(g)+12C_2H_2(g)+6C(s)$$

$Ag_2O(s)$ and $C(s)$ form the left over residue in the pan. Stoichiometric calculation for [AgppNO$_3$]$_2$, [AgmppNO$_3$]$_2$ and [AgdmppNO$_3$]$_2$ should leave a
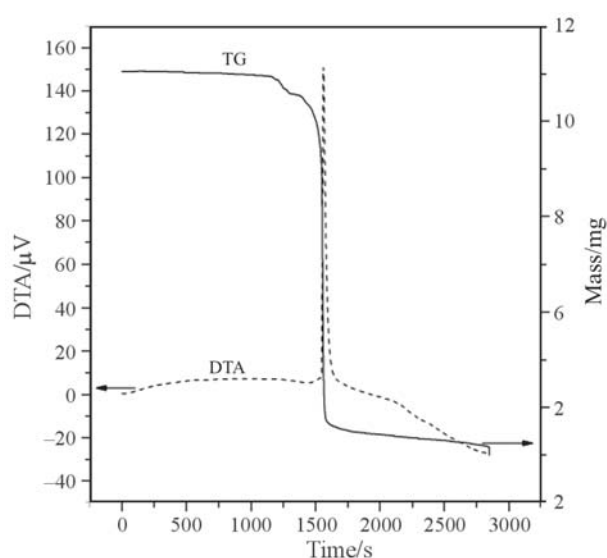
theoretical residue of 50.89, 42.99 and 34.74%, respectively. The experimental values obtained were 51.38±1.12, 42.71±0.76 and 33.46±1.33%, respectively. This consistency proves thermal decomposition of the complexes to be similar to those of the explosive material. Similar results were obtained under O_2 atmosphere [50 mL min^{-1}, 5 bars] as seen from the TG-DTA curve obtained for [AgdmppNO$_3$]$_2$ in Fig. 6.

The fact that the thermal inner reaction temperature increases with increasing hydrogen number is an important result. The reaction takes place between 246–255°C for [AgppNO$_3$]$_2$, 282–284°C for [AgmppNO$_3$]$_2$ and 299–315°C for [AgdmppNO$_3$]$_2$ the reason being activation of the aromatic rings of the ligand. As the methylene group activates the aromatic rings, with increasing number the aromatic characteristics also increases, resulting in an increase in the thermal resistance.

The exothermic heat of decomposition is seen to decrease with hydrogen number as seen from the DSC curves (Fig. 5). The hydrogen number decreases the amount of residue and increases the amount of gas evolution in accordance with the hydrogen number as observed from the thermal decomposition reactions given above. The DSC data are in correlation with these results. As the amount of gas evolved increases the residual left over is seen to decrease. As a result a decrease in the enthalpy of chemical reaction is expected with the formation of stale gas according to the law of Hess.

Acknowledgements

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Fig. 6 TG-DTA curve of [AgdmppNO$_3$]$_2$ under oxygen atmosphere

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