# Thermal decomposition of linear tetranuclear copper(II) complexes including μ-azido bridges

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**Abstract** In the first instance, mononuclear Cu(II) complexes are prepared with bis-*N*,*N*′(salicylidene)-1.3-propanediamine and derivatives. After that, these mononuclear complexes are combined with μ-bridges, by the help of azide ions, to obtain the tetranuclear complexes. Prepared complexes are characterised using IR spectroscopy, elemental analysis, and X-Ray techniques. In addition, the complexes are further analysed via TG and DSC. Molecular models of two of the nine prepared complexes are determined using X-Ray diffraction methods. The two terminal copper ions are observed to be in square pyramide coordination sphere between two oxygens of the organic ligand, two iminic nitrogens and an oxygen of the solvent while the other two cupper ions are observed to be in square pyramide coordination sphere between the fenolic oxygens of the organic ligand and the nitrogen donors of the three azide ions. It is found that the fenolic oxygens form μ-bridge and two azide ions are monodentate coordinated. In the TG analyses, the complexes are observed to decompose in a highly exothermic manner at about 200 °C. This thermal reaction is partially similar to that of explosive molecules and the data from DSC proved that the liberated heat is at explosive material levels.

**Keywords** Azide containing complexes · Explosives · Molecular structure · TG

## Introduction

The fact that azide ions form two types of μ-bridges and their tendency combine metal ions within complexes has been known since 1986 [1–10]. Also bis *N*,*N*′(salicylidene)-1,3-propanediamine type ligands are known to form polynuclear complexes with transition metals and ions like nitrate and acetate [11–17]. Mononuclear Cu(II) complexes were prepared from three ONNO type Schiff base compounds in order to synthesize polynuclear Cu(II) complexes [18–20] (Fig. 1).

Mononuclear complexes tend to form dinuclear complexes with excess Cu(II) salts [21]. Thus excess Cu(II) and equivalent $N_3^-$ were added to the solution. A dark brown crystalline precipitate was obtained. The structure was analyzed using X-ray and characterized using IR, elemental analysis and thermogravimetry. Similar studies are reported in literature [22, 23]. Reports show linear polymeric structures to form with Hg as the central atom via end–end formation of the azide ions. In the case of Cu(II) end-on bonding occurs forming tetranuclear complexes [24]. The solvent molecules are reported to be coordinated to the terminal Cu(II) ions. Thus we have chosen THF, dioxane and DMF as the solvent media. The stochiometry of the complexes prepared obtained from the thermal and elemental analysis.

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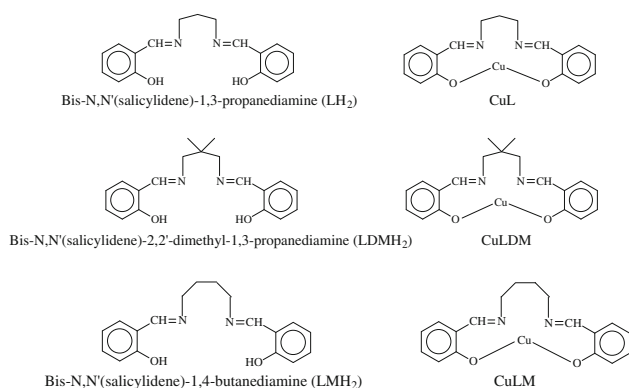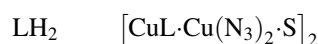Hacettepe University, Beytepe, Ankara, Turkey

**Fig. 1** The chemical formulas of three ONNO type Schiff bases and their Cu(II) complexes

$$LH_2 \qquad [CuL \cdot Cu(N_3)_2 \cdot S]_2$$

S: DMF (I), Dioxane (II), THF (III)

$$LMH_2 \qquad [CuLM \cdot Cu(N_3)_2 \cdot S]_2$$

S: DMF (IV), Dioxane (V), THF (VI)

$$LDMH_2 \quad [CuLDM \cdot Cu(N_3)_2 \cdot S]_2$$

S: DMF (VII), Dioxane (VIII), THF (IX)

Molecular models were obtained using X-ray diffraction for $[CuL \cdot Cu(N_3)_2 \cdot DMF]_2$ (I) and $[CuL \cdot Cu(N_3)_2 \cdot dioxane]_2$ (III). As stated before TG is an efficient method in determination of complex stochiometry. Thus solvent molecules and stochiometry were derived using TG.

## Experimental

### Apparatus

IR spectrums were obtained with a Mattson FTIR 1000 with KBr disks. Cu analysis was performed by dissolving a few milligram of the samples in $H_2O_2$:$HNO_3$ mixture, followed by analysis using a GBC Avanta PM model AAS. As azide ions tend to explode elemental analysis was not very efficient and thermogravimetry was used instead. TG studies were performed on a Shimadzu DTG-60H instrument within a temperature range of 25–850 °C in $N_2$ atmosphere with a heating rate of 10 °C min$^{-1}$. The exothermic heat evolved during decomposition of azide ions was measured on a DSC-60 instrument.

### X-ray crystal structure analysis

For the crystal structure determination, the single-crystal of the compounds **I** and **II** were used for data collection on a Enraf-Nonius CAD4 diffractometer [25] with MoK$_\alpha$ ($\lambda =$

0.71073 Å) radiation using the $\omega/2\theta$ scan mode. The cell parameters were determined from least-squares analysis using 25 centered reflections in the range $3.36° \leq \theta \leq 25.21°$ for compound **I** and $2.51° \leq \theta \leq 26.30°$ for compound **II**. Three standard reflections were periodically measured (every 120 min) during data collection and showed no significant intensity variations. The structures were solved by direct methods (SHELXS-97) [26] and non-H atoms were refined by full-matrix least-squares method with anisotropic temperature factors (SHELXL-97) [26] in the WinGX package [27]. A PLATON drawing [28] of the compounds **I** and **II** with 50% probability displacement thermal ellipsoids and atomic numbering scheme are shown in Fig. 2a, b. Crystal and experimental data, selected bond lengths and angles of the trimeric complexes **I** $[CuL \cdot Cu(N_3)_2 \cdot DMF]_2$ and **II** $[CuL \cdot Cu(N_3)_2 \cdot dioxane]_2$ are given in Tables 1, 2, 3, respectively.

### Preparation of complexes

They were prepared in two steps. In the first step mononuclear complexes were prepared followed by the second step where the polynuclear complexes were synthesized.

*First step*: 0.005 moles of the Schiff base (1.41 g $LH_2$, 1.515 g $LDMH_2$ or 1.48 g $LMH_2$) was dissolved in EtOH. One milliliter of $Et_3N$ was added to this solution followed
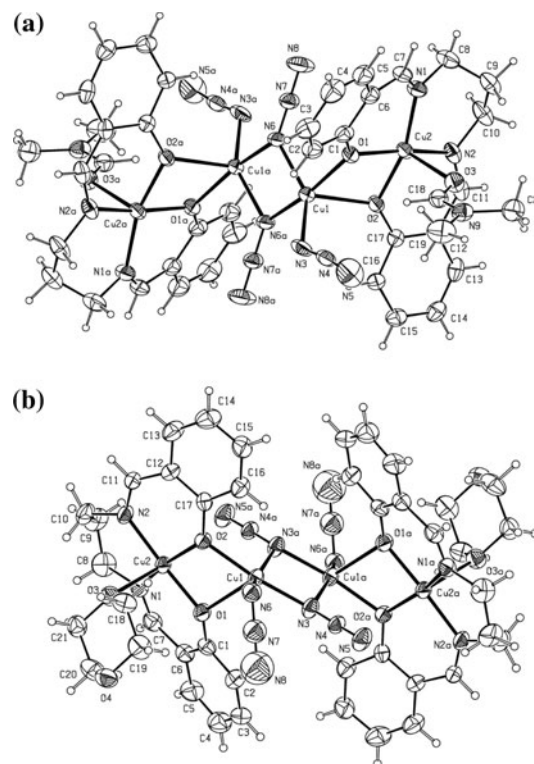


**Fig. 2 a** Platon drawing of $[CuL \cdot Cu(N_3)_2 \cdot DMF]_2$ (**I**). **b** Platon drawing of $[CuL \cdot Cu(N_3)_2 \cdot dioxane]_2$ (**II**)

**Table 1** Crystal and experimental data

| | I | II |
|---|---|---|
| Chemical formula | $C_{40}H_{46}Cu_4N_{16}O_8$ | $C_{42}H_{48}Cu_4N_{16}O_8$ |
| Formula weight | 1129.1 | 1159.1 |
| Temperature (K) | 293(2) | 293(2) |
| Wavelength (Å) | 0.71073 | 0.71073 |
| Crystal system, space group | Triclinic, P-1 | Monoclinic, P21/n |
| $a$ | 9.2110(10) | 11.2922(12) |
| $b$ | 10.3940(20) | 15.4136(11) |
| $c$ | 12.9410(10) | 13.6107(13) |
| $\alpha$ | 77.831(1) | 90 |
| $\beta$ | 92.293(2) | 97.402(5)° |
| $\gamma$ | 71.104(1) | 90 |
| Volume (Å$^3$) | 1142.94(6) | 2349.25(16) |
| Z | 1 | 2 |
| Calculated density (g cm$^{-3}$) | 1.64 | 1.64 |
| Absorbtion coefficient (mm$^{-1}$) | 1.904 | 1.856 |
| $F(000)$ | 576 | 1184 |
| Crystal size (mm) | 0.40 × 0.30 × 0.20 | 0.40 × 0.30 × 0.20 |
| $\theta_{max}$ (°) | 50.4 | 52.6 |
| Index range | $0 \leq h \leq 11$, $-11 \leq k \leq 12$, $-15 \leq l \leq 15$ | $-14 \leq h \leq 0$, $0 \leq k \leq 19$, $-16 \leq l \leq 16$ |
| Number of reflections used | 3,194, $I > 2\sigma(I)$ | 2,575, $I > 2\sigma(I)$ |
| Number of parameters | 308 | 293 |
| $R_{int}$ | 0.032 | 0.028 |
| $R$ | 0.037 | 0.07 |
| $R_w$ | 0.056 | 0.164 |
| Goodness of fit | 1.12 | 1.03 |
| $\Delta\rho_{min}$, $\Delta\rho_{max}$ (e Å$^{-3}$) | −0.339/0.729 | −1.139/1.370 |

**Table 2** Selected bond lengths (Å) of the compounds (CuLDM·Cu(N$_3$)$_2$·DMF) (**I**) and (CuLDM·Cu(N$_3$)$_2$·dioxane) (**II**)

| [CuL·Cu(N$_3$)$_2$·DMF]$_2$ (**I**) | | | | | | [CuL·Cu(N$_3$)$_2$·dioxane]$_2$ (**II**) | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Cu1 | Cu2 | 3.1501(7) | Cu2 | O2 | 1.912(5) | Cu1 | Cu2 | 3.1582(15) | Cu1 | Cu1a | 3.1156(15) |
| Cu1 | Cu1a | 3.1462(7) | Cu2 | O3 | 2.362(6) | Cu1 | O1 | 2.241(6) | Cu2 | O3 | 2.486(5) |
| Cu1 | O1 | 1.997(5) | Cu2 | N1 | 1.961(7) | Cu1 | O2 | 1.999(6) | Cu2 | N1 | 1.989(7) |
| Cu1 | O2 | 2.222(5) | Cu2 | N2 | 1.976(7) | Cu1 | N3 | 1.968(7) | Cu2 | N2 | 1.954(7) |
| Cu1 | N3 | 1.981(9) | N3 | N4 | 1.076(11) | Cu1 | N3a | 2.037(8) | N3 | N4 | 1.214(10) |
| Cu1 | N6 | 2.020(6) | N4 | N5 | 1.184(15) | Cu1 | N6 | 1.9676(10) | N4 | N5 | 1.123(10) |
| Cu1 | N6a | 2.014(6) | N6 | N7 | 1.190(9) | Cu2 | O1 | 1.912(6) | N6 | N7 | 1.2107(8) |
| Cu2 | O1 | 1.980(5) | N7 | N8 | 1.123(10) | Cu2 | O2 | 1.967(5) | N7 | N8 | 1.1523(10) |

by the addition of the solution of 0.005 mole CuCl$_2$·2H$_2$O in 50 mL of water. The mixture was left to stand for 2 days. The mononuclear complex crystals were filtered and dried in open air.

*Second step*: 0.001 mole of CuL, CuLDM or CuLM were dissolved in 30 mL DMF or 40 mL dioxane or 50 mL THF. To this was added to solutions of 0.001 mole CuCl$_2$·2H$_2$O in 20 mL hot MeOH and 0.002 mole (0.130 g) NaN$_3$ in 5 mL

hot water. The mixture was left to stand for 2–3 day and the precipitate filtered.

## Results and discussion

IR data and Cu analysis results are given in Table 4. The $\nu_{C=O}$ vibration of the DMF molecules are seen between

**Table 3** Selected bond angles (°) of the compounds [CuL·Cu(N₃)₂·DMF]₂ (**I**) and [CuL·Cu(N₃)₂·dioxane]₂ (**II**)

[CuL·Cu(N₃)₂·DMF]₂ (**I**)[a]

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Cu1a | N6 | Cu1 | 102.5(2) | O1 | Cu2 | O3 | 93.4(2) |
| Cu2 | O1 | Cu1 | 104.8(2) | O2 | Cu2 | O1 | 79.1(2) |
| Cu2 | O2 | Cu1 | 99.0(2) | O2 | Cu2 | O3 | 100.9(2) |
| O1 | Cu1 | N3 | 102.6(3) | O2 | Cu2 | N1 | 164.1(3) |
| O1 | Cu1 | N6a | 164.0(2) | O2 | Cu2 | N2 | 91.5(3) |
| O1 | Cu1 | N6 | 90.0(2) | N1 | Cu2 | N2 | 98.4(3) |
| O1 | Cu1 | O2 | 71.7(2) | N1 | Cu2 | O1 | 90.0(3) |
| N3 | Cu1 | N6a | 93.3(3) | N2 | Cu2 | O1 | 169.9(2) |
| N3 | Cu1 | N6 | 148.2(4) | N1 | Cu2 | O3 | 91.2(3) |
| N6a | Cu1 | N6 | 77.5(2) | N2 | Cu2 | O3 | 92.1(3) |
| N3 | Cu1 | O2 | 102.3(3) | N8 | N7 | N6 | 178.8(12) |
| N6a | Cu1 | O2 | 102.8(2) | N3 | N4 | N5 | 173.7(11) |
| N6 | Cu1 | O2 | 109.4(3) | | | | |

[CuL·Cu(N₃)₂·dioxane]₂ (**II**)[b]

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Cu1 | N3 | Cu1a | 102.1(3) | O2 | Cu1 | N3a | 90.1(3) |
| Cu2 | O1 | Cu1 | 98.7(2) | O1 | Cu2 | N2 | 169.2(3) |
| Cu2 | O2 | Cu1 | 105.6(2) | O1 | Cu2 | O2 | 80.0(2) |
| O2 | Cu1 | O1 | 71.9(2) | N2 | Cu2 | O2 | 90.9(3) |
| N3 | Cu1 | O2 | 167.9(3) | O1 | Cu2 | N1 | 92.7(3) |
| N6 | Cu1 | O2 | 92.73(18) | N2 | Cu2 | N1 | 97.6(3) |
| N3 | Cu1 | O1 | 107.9(3) | O2 | Cu2 | N1 | 161.4(3) |
| N3a | Cu1 | O1 | 93.3(3) | N4 | N3 | Cu1 | 129.9(7) |
| N6 | Cu1 | O1 | 108.22(18) | N4 | N3 | Cu1a | 120.0(6) |
| N3 | Cu1 | N6 | 98.7(2) | N5 | N4 | N3 | 178.3(10) |
| N3 | Cu1 | N3a | 77.9(3) | N7 | N6 | Cu1 | 107.72(3) |
| N6 | Cu1 | N3a | 158.1(2) | N8 | N7 | N6 | 176.8(3) |

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

[b] Symmetry code: (a) $1 - x, 1 - y, 1 - z$

1,654 and 1,649 cm⁻¹, whereas the $\nu_{C=N}$ stretching of the ligands is seen between 1,620 and 1,627 cm⁻¹. $\nu_{C=N}$ band seen at 1,640 cm⁻¹ for the ligand shifts by 15 cm⁻¹ to lower energy level [29–31]. N₃⁻ ions are observed clearly at 2,200 cm⁻¹. Azide ions form two types of μ-bridges 1,1 (end–on) and 1,3 (end–end). The double bond structure should be the case in both μ-bridge structures (Fig. 3).

The triple bond structure is observed at 2,200 cm⁻¹, but the double bond structure shifts to lower energy values [9, 32]. These can be observed in the complexes. The $\nu_{N_3}$ bonds show at least the presence of one μ-bridge as two vibration at 2,034 and 2,071 cm⁻¹ are observed. But IR does not show the structure of the bridge. Literature states this bridge to be of 1.1 structure [32–34]. The Platon drawing of [CuL-DM·Cu(N₃)₂·DMF]₂ and [CuLDM·Cu(N₃)₂·dioxane]₂ are given in Fig. 2a and b, respectively.

Figure 2 shows a tetranuclear structure with two CuL-DM·Cu(N₃)₂ units bonded by a 1,1 μ-bridge and two free azide ions. A μ-bridge between CuLDM and Cu(N₃)₂ is found via the phenolic oxygens. In the terminal CuLDM unit the Cu(II) ion situated between the ON1N2O2 donor atom is coordinated by a THF molecule. The coordination sphere of the four Cu(II) ions is a square pyramid (Fig. 4).

The ideal structure of penta coordinated structures is measured by a $\tau$ value [30].

$$\tau = \frac{\alpha - \beta}{60}$$

$\alpha$ and $\beta$ are the largest angles in the vicinity of the central ions. If $\tau = 0$ the coordination is an ideal square pyramid, if $\tau = 1$ it is an ideal trigonal bipyramid. Crystal data of complex I and complex III are given in Table 1 whereas important coordinative bond lengths and bond angels are given in Tables 2 and 3. The $\alpha$ and $\beta$ values of Cu1 are 164.0(2)° and 148.2(4)° and 169.9(2)° and 164.1(3)°, respectively for complex I. In this case $\tau$ value for Cu1 is 0.263 and 0.093 for Cu2. These values can calculate for complex III as 0.163 and 0.130, respectively and these values indicate the coordination sphere to be a distorted square pyramid. The basal plane of the Cu2 ion coordination sphere are the O1N1N2O2 atoms, because Cu2 is 0.1326 Å in distance from this plane for the complex I and 0.1104 Å for complex III. The Cu2–O3 distance is 2.362(5) Å and is clearly further than the Cu2–N1, Cu2–O2 and Cu2–N2 distances fort he complex I. This means the Cu2 coordination sphere has elongated towards the THF oxygen.

Thermoanalytical data of the complexes have been given in Table 5. TG and DTA curves are shown in Fig. 5a–e, respectively. The figures reveal three thermal reactions; mass loss between 120 and 170 °C, exothermic mass loss between 200 and 210 °C and degradation around 260 °C. The first reaction corresponds to separation of coordinated solvent molecules from the structure. The mass loss coincides with the mass loss of these molecules. THF leaves the structure at 120 °C, dioxane between 135 and 140 °C and DMF between 160 and 170 °C. The second thermal reaction is due to the explosive reaction of the azide ions according to the our recently work [35]. After this reaction the TG curves resembles that of CuL. Above 260 °C degradation of the compound continues. In all complexes the TG curves resemble that of CuL above 210 °C [36–38]. The explosive reaction does not destroy the whole molecule. The remaining CuL decomposes with increasing temperature. The mass loss during the explosive reaction is higher than expected and is probably due to scattering of the molecules. Also above 750 °C oxygen was purged into the system and residue converted to CuO, but the remaining mass loss of CuO does not correspond to the expected amount. The question "Does the tetranuclear complex decompose after separation of the solvent molecules?" crises. The terminal Schiff base-Cu(II) complex bonds to Cu(N₃)₂ via the phenolic oxygens, resulting in a

**Table 4** Cu analysis and important IR data of the complexes

| Complex | Cu analysis | | Important IR bands (cm$^{-1}$) | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Expected % | Found % | $\nu_{C-H\,(Ar)}$ | $\nu_{C-H\,(Aliph)}$ | $\nu_{N_3}$ | $\nu_{C=O}$ | $\nu_{C=N}$ | $\nu_{C=C}$ | $\delta_{CH_2}$ | $\delta_{C-H\,(Ar)}$ |
| [CuL·Cu(N$_3$)$_2$·DMF]$_2$ (**I**) | 22.52 | 22.16 | 3,019 | 2,869 | 2,081 | 1,651 | 1,632 | 1,596 | 1,468 | 752 |
| | | | 3,047 | 2,931 | 2,039 | | | | | |
| [CuL·Cu(N$_3$)$_2$·dioxane]$_2$ (**II**) | 21.93 | 22.08 | 3,027 | 2,860 | 2,086 | – | 1,629 | 1,599 | 1,471 | 754 |
| | | | 3,058 | 2,927 | 2,034 | | | | | |
| [CuL·Cu(N$_3$)$_2$·THF]$_2$ (**III**) | 22.55 | 22.27 | 3,021 | 2,857 | 2,079 | – | 1,634 | 1,598 | 1,471 | 756 |
| | | | 3,055 | 2,938 | 2,031 | | | | | |
| [CuLDM·Cu(N$_3$)$_2$·DMF]$_2$ (**IV**) | 21.32 | 20.97 | 3,024 | 2,828 | 2,081 | 1,652 | 1,631 | 1,604 | 1,471 | 757 |
| | | | 3,055 | 2,978 | 2,036 | | | | | |
| [CuLDM·Cu(N$_3$)$_2$·dioxane]$_2$ (**V**) | 20.79 | 21.24 | 3,022 | 2,831 | 2,079 | – | 1,630 | 1,601 | 1,468 | 756 |
| | | | 3,057 | 2,974 | 2,033 | | | | | |
| [CuLDM·Cu(N$_3$)$_2$·THF]$_2$ (**VI**) | 21.35 | 20.57 | 3,028 | 2,826 | 2,086 | – | 1,630 | 1,602 | 1,470 | 757 |
| | | | 3,061 | 2,971 | 2,033 | | | | | |
| [CuLM·Cu(N$_3$)$_2$·DMF]$_2$ (**VII**) | 21.97 | 21.51 | 3,022 | 2,834 | 2,084 | 1,650 | 1,631 | 1,599 | 1,472 | 756 |
| | | | 3,057 | 2,968 | 2,035 | | | | | |
| [CuLM·Cu(N$_3$)$_2$·dioxane]$_2$ (**VIII**) | 21.41 | 21.33 | 3,025 | 2,833 | 2,086 | – | 1,632 | 1,601 | 1,474 | 754 |
| | | | 3,054 | 2,972 | 2,037 | | | | | |
| [CuLM·Cu(N$_3$)$_2$·THF]$_2$ (**IX**) | 22.00 | 21.46 | 3,024 | 2,834 | 2,084 | – | 1,630 | 1,602 | 1,475 | 757 |
| | | | 3,056 | 2,972 | 2,035 | | | | | |
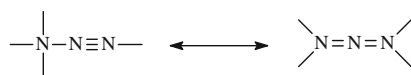


**Fig. 3** Resonance structures of azide ions



S= DMF, THF, Dioxane   R= ——(CH$_2$)$_3$—— , ——(CH$_2$)$_4$—— , ——CH$_2$—C(CH$_3$)$_2$—CH$_2$——
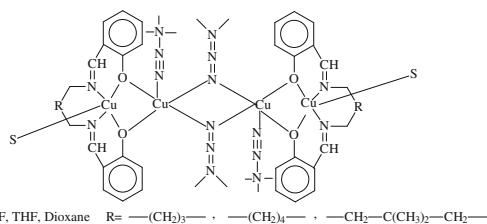
**Fig. 4** The chemical formulas of the complexes

decrease of electron density given to Cu(II) ions from the phenolic oxygens. The terminal Cu(II) ion completes the electron deficiency from solvent molecules by coordinating them. If this coordination is damaged then the $\mu$-bridges can break.

$$[CuL \cdot Cu(N_3)_2 \cdot S]_2 \xrightarrow[-2S]{[\quad]} 2CuL + 2Cu(N_3)_2$$
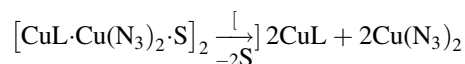
In the remaining mixture Cu(N$_3$)$_2$ undergoes an explosive reaction and the remaining CuL decomposes between 260 and 300 °C. TG measurements do not explain this.

With the explosion of Cu(N$_3$)$_2$ a portion of CuL disintegrates. The remaining mass after 300 °C is a random mass. We think it is comprised randomly of a mixture CuO and carbonized ports, because the mass loss in the vicinity of 300 °C is the larger than the CuO amount. DSC measurements show the explosion to spread throughout the molecule. For reference Cu(N$_3$)$_2$ was prepared and the heat values measured; $1.32 \pm 0.04$ kJ g$^{-1}$ or 194.76 kJ mol$^{-1}$. If after separation of the solvent molecules Cu(N$_3$)$_2$ is formed the value of heat obtained from DSC should equal the mass fraction of Cu(N$_3$)$_2$ in the complex and the explosion heat of this compound. But the values obtained are higher than expected. The mass ratio of Cu(N$_3$)$_2$ in [CuL·Cu(N$_3$)$_2$·dioxane]$_2$ and [CuL·Cu(N$_3$)$_2$·DMF]$_2$ are 0.254 and 0.261, respectively. The expected heat value for [CuL·Cu(N$_3$)$_2$·dioxane]$_2$ is 335.25 and 349.52 J g$^{-1}$ for [CuL·Cu(N$_3$)$_2$·DMF]$_2$. but DSC data were 607.21 and 558.04 J g$^{-1}$, respectively. This shows the complex does not decompose after separation of the solvent molecules. Cu(N$_3$)$_2$ has spread its explosive characteristic throughout the molecule. This can be seen from the DTA peak. The peak maximum of Cu(N$_3$)$_2$ is between 199 and 201 °C, but within the complex this value shifts to 210–222 °C. This shows that when $\mu$-bridges are formed with azide ions the explosive character does not decrease within the complex structure but, all of the complex structure tends to become an explosive material alternative.

**Table 5** Thermoanalytical data of the complexes

| Complex | First thermal reaction Loss of coordinated solvent | | | Second thermal reaction Decomposition of azide | | | Third thermal reaction Decomposition of complex | | |
|---|---|---|---|---|---|---|---|---|---|
| | Temp. range (°C) | Expected mass loss (%) | Mass loss found (%) | Temp. range (°C) | Expected mass loss (%) | Mass loss found (%) | Temp. range (°C) | Expected % residue | Found % residue |
| $[CuL \cdot Cu(N_3)_2 \cdot DMF]_2$ (**I**) | 137–178 DTG: 153 | 12.93 | 13.35 ± 0.44 | 199–229 DTG: 204 | 26.14 | 45.01 ± 1.58 | 262–324 | 14.10 | 24.54 ± 2.04 |
| $[CuL \cdot Cu(N_3)_2 \cdot dioxane]_2$ (**II**) | 130–171 DTG: 139 | 15.20 | 12.98 ± 0.84 | DTG: 234 | 25.46 | 55.95 ± 4.47 | 260–337 | 13.73 | 18.11 ± 1.38 |
| $[CuL \cdot Cu(N_3)_2 \cdot THF]_2$ (**III**) | 128–160 DTG: 144 | 12.79 | 12.28 ± 0.92 | 189–229 DTG: 221 | 26.18 | 51.40 ± 5.16 | 258–334 | 14.13 | 22.86 ± 3.16 |
| $[CuLDM \cdot Cu(N_3)_2 \cdot DMF]_2$ (**IV**) | 139–171 DTG: 148 | 12.25 | 11.75 ± 0.74 | 201–244 DTG: 238 | 24.76 | 46.07 ± 4.12 | 256–341 | 13.76 | 16.74 ± 1.86 |
| $[CuLDM \cdot Cu(N_3)_2 \cdot dioxane]_2$ (**V**) | 131–184 DTG: 148 | 14.42 | 14.69 ± 1.57 | 194–216 DTG: 208 | 24.14 | 32.12 ± 1.82 | 254–336 | 13.41 | 29.68 ± 1.48 |
| $[CuLDM \cdot Cu(N_3)_2 \cdot THF]_2$ (**VI**) | 93–172 DTG:135 | 11.80 | 11.06 ± 1.34 | 191–209 DTG:201 | 24.79 | 32.69 ± 2.24 | 251–334 | 13.78 | 26.32 ± 1.20 |
| $[CuLM \cdot Cu(N_3)_2 \cdot DMF]_2$ (**VII**) | 101–174 DTG: 128 | 12.62 | 11.89 ± 1.04 | 196–228 DTG: 202 | 25.50 | 32.03 ± 1.16 | 249–334 | 13.92 | 25.53 ± 1.34 |
| $[CuLM \cdot Cu(N_3)_2 \cdot dioxane]_2$ (**VIII**) | 82–177 DTG: – | 14.85 | 13.59 ± 1.22 | 184–224 DTG: 190 | 24.86 | 37.86 ± 1.27 | 242–322 | 13.57 | 25.96 ± 0.88 |
| $[CuLM \cdot Cu(N_3)_2 \cdot THF]_2$ (**IX**) | 77–168 DTG: – | 12.48 | 13.93 ± 0.45 | 191–219 DTG: 201 | 25.54 | 28.60 ± 1.21 | 286–329 | 13.95 | 26.42 ± 1.70 |
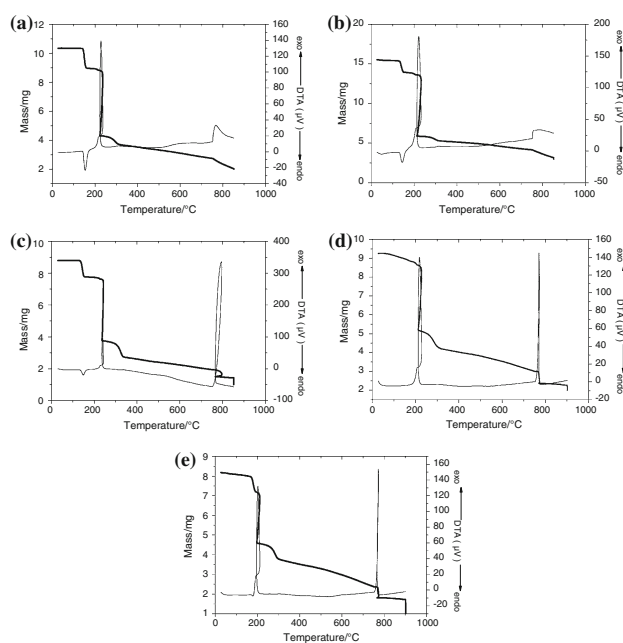


**Fig. 5** The TG curve of **a** [CuL·CuN₃·DMF]₂, **b** [CuL·CuN₃·THF]₂, **c** [CuLDM·CuN₃·DMF]₂, **d** CuL 1–4 CuN₃·dioxane, and **e** CuL 1–4 CuN₃·THF

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