

New Energetic Copper(II) Complexes With Pyrazolyl Type Ligands

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Abstract. Nine Cu^{II} complexes (**I–IX**) containing the azide ion and bis-2,6-(pyrazol-1-yl)pyridine (pp), bis-2,6-(pyrazol-1-yl)pyridine (dmpp), and 2-(pyrazol-1-yl)-6-(3,5-dimethylpyrazol-1-yl)pyridine (mpp), which are derivatives of pyrazolylpyridine, were prepared in nonaqueous medium. These complexes were characterized by elemental analyses and IR spectroscopy. Crystals of one of these complexes [CumpClN₃ (**VII**)] were prepared in suitable size, and a molecular

structure of this complex was obtained with X-ray diffraction method. Complexes were examined by thermogravimetry and differential scanning calorimetry methods. Thermal decomposition was observed in complexes including two azide groups similar to that seen in explosives. In the complexes containing one azide group, formation of the Cu^I complexes was observed after thermal decomposition of the azide group.

Introduction

Bis-2,6-(3,5-dimethylpyrazol-1-yl)pyridine is an *NNN*-type ligand known since 1980.^[1, 2] It is frequently used in coordination chemistry since it is a terpyridyl-like ligand. Cu^{II},^[3–5] Co^{II},^[6, 7] gold, platinum,^[8] Ni^{II},^[9] silver^[10, 11] and many Fe^{II} complexes with pyrazolylpyridine ligands were reported.^[12] Moreover, there are also reports mentioning Ru^{III} complexes^[13] and titanium complexes,^[14] with catalytic properties. In this study, bis-2,6-(pyrazol-1-yl)pyridine (dmpp) with symmetrical structure and 2-(pyrazol-1-yl)-6-(3,5-dimethylpyrazol-1-yl)pyridine (mpp) with asymmetrical structure were used as ligands. Figure 1 illustrates the open structure of these ligands.

It was known from previous studies that complexes are formed with Cu^{II} and these ligands depending on the anion in the medium.^[4, 15, 16] Accordingly, an azide ion was added to the environment so that mole ratio of the pyrazole ligand would be

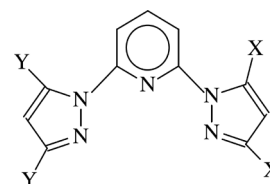


Figure 1. Open structure of the prepared ligands. X = Y = H (pp), X = Y = CH₃ (dmpp), X = CH₃, Y = H (mpp).

1:1 and 1:2 within the nonaqueous solution and the following complexes were obtained:

- CuppClN₃ (**I**)
- CuppNO₃N₃ (**II**)
- Cupp(N₃)₂ (**III**)
- CudmppClN₃ (**IV**)
- CudmppNO₃N₃ (**V**)
- Cudmpp(N₃)₂ (**VI**)
- CumpClN₃ (**VII**)
- CumpNO₃N₃ (**VIII**)
- Cump(N₃)₂ (**IX**)

Elemental analyses and IR spectroscopy were used to determine the stoichiometry of these complexes.

CuCl₂·2H₂O and Cu(NO₃)₂·3H₂O were used for the formation of complexes. The reason for using Cu(NO₃)₂·3H₂O is the oxidizing property of the nitrate group. Alternative explosive characteristics of the pyrazolyl complexes with AgNO₃ prepared in the previous studies were reported.^[10, 11]

These complexes contain azide, and are rich in nitrogen. Because of this reason, these complexes are thought to be energetic complexes, and they were examined by thermogravimetry (TG) and differential scanning calorimetry (DSC). Only single crystals of complex **VII** were obtained and the molecular structure was determined by X-ray diffraction studies.

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Table 1. Results of elemental analyses and selected IR data of prepared complexes.

Ligand or Complex	Elemental Analyses					IR /cm ⁻¹									
	Calculated /%					Experimental /%					$\gamma_{\text{CH(Ar)}}$	$\gamma_{\text{CH(Aliph)}}$	γ_{N3}	$\gamma_{\text{C=N (Ring)}}$	$\gamma_{\text{C=C (Ring)}}$
	C	H	N	Cl	Cu	C	H	N	Cl	Cu					
pp	62.55	4.29	33.15	—	—	62.41	4.67	33.09	—	—	3171–3114	—	—	1605	1590
mpp	65.26	5.47	29.26	—	—	65.77	5.11	28.07	—	—	3163–3103	2931–2870	—	1604	1582
dmpp	67.40	6.41	26.19	—	—	66.79	5.96	27.10	—	—	3165–3097	2933–2864	—	1601	1587
I	37.51	2.57	31.80	10.07	18.04	37.93	3.12	31.24	9.86	17.72	3134–3062	—	2058–2083	1622	1589
II	31.85	3.16	30.38	—	15.32	30.56	3.27	28.19	—	15.64	3109–3055	—	2040	1620	1591
III	36.83	2.53	42.93	—	17.71	36.65	3.04	41.76	—	16.95	3147–3066	—	2054–2079	1611	1590
IV	44.12	4.19	27.43	8.68	15.56	43.86	4.22	25.69	7.47	14.83	3142–3062	2928–2869	2044–2058	1622	1590
V	39.78	4.23	27.82	—	14.03	38.84	4.49	26.54	—	14.19	3134–3056	2926–2964	2052	1609	1593
VI	43.42	4.13	37.12	—	15.31	42.90	4.35	36.41	—	15.08	3138–3064	2930	2051–2077	1610	1588
VII	41.06	3.45	29.46	9.32	16.71	40.59	4.10	28.82	8.82	15.92	3130–3061	2930	2054	1616	1591
VIII	38.38	3.22	30.97	—	15.62	38.12	3.73	30.42	—	15.23	3117–3059	2931	2058	1614	1590
IX	40.36	3.38	39.82	—	16.43	40.41	3.55	39.14	—	15.96	3145–3027	2933	2081–2065	1620	1589

Experimental Section

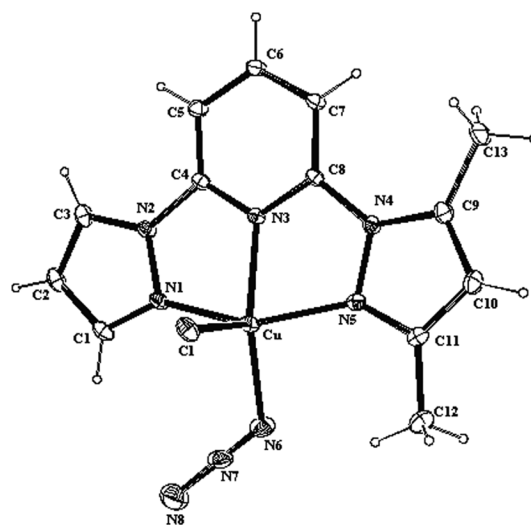
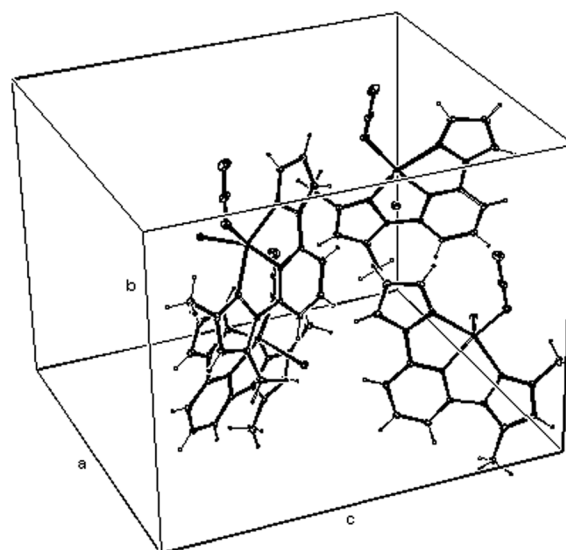
General

Eurovector 3018 C,H,N,S analyzer was used for elemental analyses for C, H and N. Cl analyses were performed with AgNO₃ gravimetrically. Cu analyses however, were performed on GBC Avanta PM Model AAS device. For Cu analyses, the sample (2–3 mg) was digested in a solution containing HNO₃ (1.0 mL 63 %) and H₂O₂ (1.0 mL 30 %), diluted to 100 mL and directly fed into FAAS device. IR spectra were recorded by Shimadzu Infinity Model device. Shimadzu DTG 60H and DSC60 devices were used for thermal analyses, which were performed under nitrogen atmosphere with a heating rate of 10 °C·min⁻¹ and within platinum pans.

X-ray Data Collection and Structure Refinement

The crystal and instrumental parameters used in the unit-cell determination and data collection are summarized in Table 1. Diffraction measurements were made at room temperature with a Oxford Diffraction Xcalibur (TM) Single crystal X-ray Diffractometer with Sapphire CCD Detector with Mo-K α radiation ($\lambda = 0.71073$ Å), using ω -2 θ scan mode. Unit-cell dimensions were determined and refined by using the angular settings of 25 automatically centered reflections in the $2.46 \leq \theta \leq 26.37$ ranges. The structure was solved by the direct methods using SHELXS-97 and refined by full-matrix least-squares techniques on F^2 with SHELXL-97.^[17] The empirical absorption corrections were applied by the semi-empirical method by CrysAlis CCD software.^[18] Non-hydrogen atoms were anisotropic and all hydrogen atom positions were refined in an isotropic approximation in the riding model with the $U_{\text{iso}}(\text{H}) = 1.5 U_{\text{eq}}(\text{C,H})$ for methyl groups and $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{iso}}(\text{C,H})$ for other carbon atoms. An ORTEP drawing^[19] of the complex with 40 % probability displacement thermal ellipsoids, atom-labeling scheme and packaging of the molecules in the unit cell are shown in Figure 2 and Figure 3, respectively.

Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre CCDC, 12 Union Road, Cambridge CB21EZ. Copies of the data can be obtained on quoting the depository number CCDC-745491 (**VII**) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk or www://www.ccdc.cam.ac.uk).

**Figure 2.** Ortep drawing of complex **VII**.**Figure 3.** Packing of the atoms in the unit cell.

Preparation of the Ligands

Preparation was made according to pp, dmpp, and mpp literature.^[1]

Preparation of pp: Pyrazol (6.8 g, 0.1 mol) was solved in diglyme (150 mL) at room temperature. To this solution, newly-cut metallic sodium (3.9 g, 0.1 mol) was added under nitrogen and reflux, and the solution was stirred for 3–4 hours to dissolve the potassium. Subsequently, solid 2,6-dichloropyridine (7.4 g, 0.05 mol) was added to this solution, and was dissolved by heating. Temperature of the solution was raised to 110–120 °C and the solution was stirred for about 12 hours. Formation of solid NaCl was observed. After this period, the cooled solution was poured onto water-ice mixture (500 mL), and NaCl was dissolved by agitating. The colorless precipitate was filtered and dried in air.

Preparation of dmpp: Dmpp was prepared from 3,5-dimethylpyrazole (0.1 mol) and 2,6-dichloropyridine (0.05 mol) according to the procedure for preparation of pp.

Preparation of mpp: This ligand was prepared in two steps.

Step 1: Pyrazole (3.4 g, 0.05 mol) was dissolved in diglyme (150 mL) together with newly-cut metallic sodium (1.95 g, 0.05 mol). This solution was allowed to react with 2,6-dichloropyridine at a temperature of 110 °C for 6 hours. This mixture was poured onto ice water (300 mL). Afterwards, the colorless precipitate was filtered and air-dried.

Step 2: 3,5-Dimethylpyrazole (4.8 g, 0.05 mol) was dissolved in diglyme (100 mL) at room temperature. To this solution, newly-cut metallic sodium (1.95 g, 0.05 mol) was added under nitrogen and reflux, and the solution was stirred for 3–4 hours to dissolve the sodium. The substance (9.02 g, 0.05 mol) formed in step 1, was added to the solution and the solution was stirred for about 24 hours at 120–130 °C. At the end of this period, the mixture was poured into ice water (300 mL). The colorless precipitate was filtered and air-dried.

Preparation of the Complexes

CuppCl(N₃) (I), CudmppCl(N₃) (IV), and CumppCl(N₃) (VII): pp, dmpp, or mpp (0.01 mol) was dissolved in MeCN:MeOH (1:1) (50 mL) mixture by heating. To this solution, a solution of CuCl₂·2H₂O (0.01 mol) within hot MeOH (20 mL) and aqueous solution of NaN₃ (0.01 mol) in hot water (10 mL) were added, and the resulting solution was allowed to settle for 24 hours. The brown precipitate was filtered and air-dried.

Cupp(NO₃)(N₃) (II), Cudmpp(NO₃)(N₃) (V), and Cumpp(NO₃)(N₃) (VIII): According to the procedure above, organic ligand (0.01 mol), Cu(NO₃)₂·3H₂O (0.01 mol), and NaN₃ (0.01 mol) were used to prepare complexes.

Cupp(N₃)₂ (III), Cudmpp(N₃)₂ (VI), and Cumpp(N₃)₂ (IX): According to the procedure above, organic ligand (0.01 mol), CuCl₂·2H₂O (0.01 mol) and NaN₃ (0.02 mol) were used to prepare complexes.

Results and Discussion

Results of the elemental analyses and some important IR data for the ligands and complexes prepared are given in Table 1. The molecular structure of complex **VII** obtained by X-ray diffraction studies is given in Figure 2, data collection and crystal data are given in Table 2, and important bond lengths and bonding angles around the coordination sphere are given in Table 3.

Table 2. Crystal and experimental data for complex **VII**.

<i>a</i> /Å	12.7075(5)
<i>b</i> /Å	14.6951(9)
<i>c</i> /Å	16.2662(9)
α /°	90
β /°	90
γ /°	90
<i>V</i> /Å ³	3037.5(3)
<i>Z</i>	8
Cell measurement temperature	302(2)
Crystal dimensions /mm	0.22 × 0.22 × 0.03
Density (diffn) <i>d</i> /g·cm ⁻³	1.663
<i>F</i> (000)	1544
μ	1.626
<i>T</i> /K	302(2)
radiation	Mo- <i>K</i> _α
λ /Å	0.71073
Reflns number	18976
$\theta_{\max}$	0.999
$\theta_{\min}$	0.999
$h_{\min} - h_{\max}$	−15,15
$k_{\min} - k_{\max}$	−18,15
$l_{\min} - l_{\max}$	−20,16
reflns number total	3105
Reflns number gt	1299
Reflns threshold expression	>2 $\sigma(I)$
<i>R</i> _{all}	0.1268
<i>R</i>	0.0384
<i>wR</i>	0.1031
goodness of fit	0.881
$\delta_{\max}$ /e·Å ⁻³	0.492
$\delta_{\min}$ /e·Å ⁻³	−0.377

Table 3. Selected bond lengths /Å and angles /° around the coordination sphere for complex **VII**.

N1–N2	1.358(4)
N1–Cu1	2.057(3)
N3–Cu1	1.973(3)
N4–N5	1.396(4)
N5–Cu1	2.049(3)
N6–N7	1.046(6)
N6–Cu1	1.937(4)
N7–N8	1.249(7)
Cl1–Cu1	2.4797(13)
N4–N5 Cu1	113.2(3)
N7–N6 Cu1	123.4(5)
N6–N7–N8	174.6(7)
N6–Cu1–N3	159.17(18)
N6–Cu1–N5	98.17(17)
N3–Cu1–N5	77.12(14)
N6–Cu1–N1	100.47(16)
N3–Cu1–N1	78.37(14)
N5–Cu1–N1	152.70(13)
N6–Cu1–Cl1	102.65(16)
N3–Cu1–Cl1	98.07(10)
N5–Cu1–Cl1	96.66(10)
N1–Cu1–Cl1	98.50(10)

Results of the elemental analyses and molecular model indicate that the Cu^{II} ion/ligand ratio is 1:1 for all complexes. The crystal packaging diagram of complex **VII** is shown in Figure 3. It can be seen from Figure 2 and Figure 3 that the coordination arrangement around the pentacoordinate Cu^{II} ion is a

distorted square pyramid of three nitrogen atoms from the ligand, one chlorine atom, and one nitrogen atom from azide.

Since not for all complexes molecular structures could be obtained by single crystal X-ray diffraction, it would not be very accurate to propose the same coordination for all. However, five-membered coordination is one of the coordination forms encountered most frequently for Cu^{II} ions, particularly for square-pyramidal coordination sphere.^[20] The molecular structures of pentacoordinate transition metal complexes show an extensive range from regular trigonal bipyramidal to regular square pyramidal. The structural index parameter, $\tau = (\beta - \alpha/60)$, was evaluated by the two large angles in the pentacoordinate arrangement, where $\tau = 0.0$ for a regular square pyramidal, $\tau = 1.0$ for a trigonal bipyramidal arrangement ($\alpha < \beta$).^[21] The coordination arrangement around Cu^{II} is slightly distorted from regular square pyramidal, as ascertained by the observed τ value of 0.10 [$\alpha = 152.70(13)^\circ$ and $\beta = 159.17(14)^\circ$]. Coordination seems to be square pyramidal, a chlorine atom and three nitrogen atoms of the pyrazole and pyridyl ligand constitute the basal plane of the square pyramid, and the azide nitrogen atom occupies the apical position (Figure 2). The $\text{Cu}^{\text{II}}\text{--N}(\text{azide})$ distance is slightly shorter than the $\text{Cu}^{\text{II}}\text{--N}(\text{pyrazole})$ and $\text{Cu}^{\text{II}}\text{--N}(\text{pyridyl})$ distances. The average $\text{Cu}\text{--N}$ bond lengths [$2.004(3) \text{ \AA}$] are similar to those in other trans-Schiff base complexes.^[22, 23] The $\text{Cu}^{\text{II}}\text{--Cl}$ distances of $2.4798(13) \text{ \AA}$ are in well agreement with the reported $\text{Cu}^{\text{II}}\text{--Cl}$ distances.^[24] The coordination arrangement is characterized by an N1--Cu--N5 axial angle $152.70(13)^\circ$, and N3--Cu--Cl and N3--Cu--N6 equatorial angles range from $98.07(10)$ to $159.17(14)^\circ$. The two rings consisting of $(\text{Cu}, \text{N1}, \text{N2}, \text{C4}, \text{N3})$ and $(\text{Cu}, \text{N5}, \text{N4}, \text{C8}, \text{N3})$ are planar. The dihedral angles between the planes of two rings are $6.96(16)^\circ$. The copper atom lies $-0.0578(16)$ and $-0.0458(14) \text{ \AA}$ out of the $(\text{Cu}, \text{N1}, \text{N2}, \text{C4}, \text{N3})$ and $(\text{Cu}, \text{N5}, \text{N4}, \text{C8}, \text{N3})$ planes, respectively.

TG results showed that complexes **II** and **V** contain crystalline water, (Figure 4 and Figure 5).

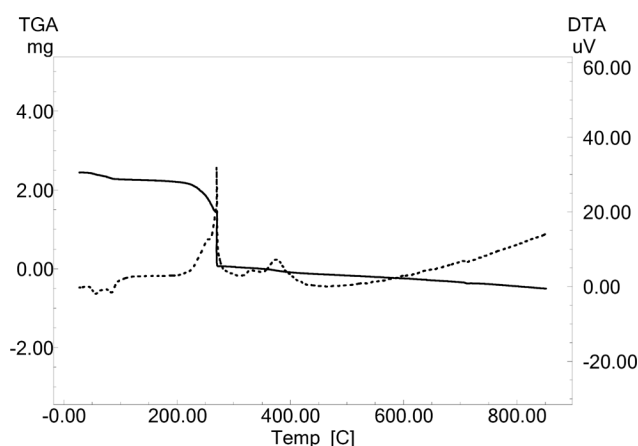


Figure 4. TG curve of $\text{Cupp}(\text{NO}_3)(\text{N}_3) \cdot 2\text{H}_2\text{O}$. — TG curve, DTA curve.

It is understood by examining the TG curves that complex **II** contains two mol of crystalline water, and complex **V** contains one mol of crystalline water. Thermoanalytical data of the nine

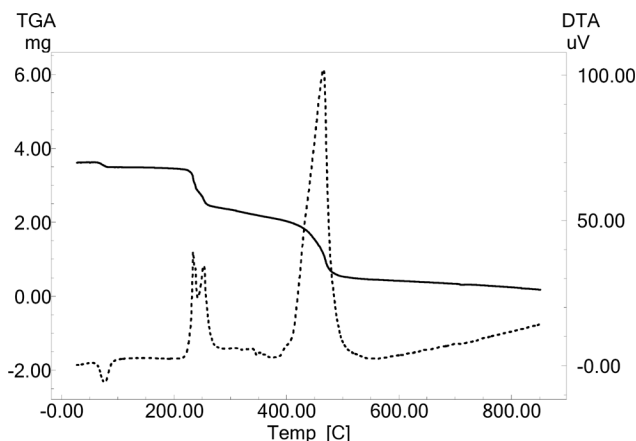


Figure 5. TG curve of $\text{Cudmpp}(\text{NO}_3)(\text{N}_3) \cdot \text{H}_2\text{O}$. — TG curve, DTA curve.

complexes can be seen in Table 4. Thermal breaking of the crystalline water seen in complexes **II** and **V** is exothermic, as expected. All the complexes give the first thermal decomposition reactions at around 200°C . This reaction can be explained based on the data in the previous literature. The first thermal reaction is the breaking of azide groups.^[25] Complexes **I**, **VI**, and **IX** contain two azide groups per Cu^{II} ion, and the mass losses for all the three complexes is over 90 % in the first thermal reaction (Figure 6), exothermal heat measured with DSC exceeds 400 kJ mol^{-1} (Figure 7). The order of the decomposition temperatures is as follows:

$\text{Cupp}(\text{N}_3)_2$ (**III**) > $\text{Cudmpp}(\text{N}_3)_2$ (**VI**) > $\text{Cumpp}(\text{N}_3)_2$ (**IX**)

Mass losses in the first thermal decomposition reaction of complexes **I**, **II**, **IV**, and **VII**, which include one chlorine atom, range between 82 and 94 %. Ligands of CuppClN_3 and CudmppClN_3 are symmetrical. Mass losses in these complexes are between 82 and 94 %, and the mass loss in the CumppClN_3 complex of the asymmetrical ligand is about 91 %. There are not any anomalies in these thermal decompositions. Azide ions constitute 10 % of the total mass. However, the mass loss rises to 90 % level in the decomposition. Probably, all the energy of the azide group is distributed within the whole complex and this causes the complex to decompose as an energetic molecule as a whole. Order of the temperatures measured by DSC is:

CudmppClN_3 (**IV**) > CumppClN_3 (**VII**) > CuppClN_3 (**I**).

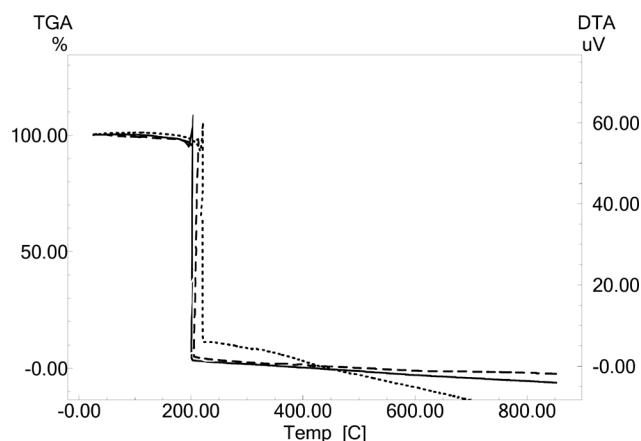
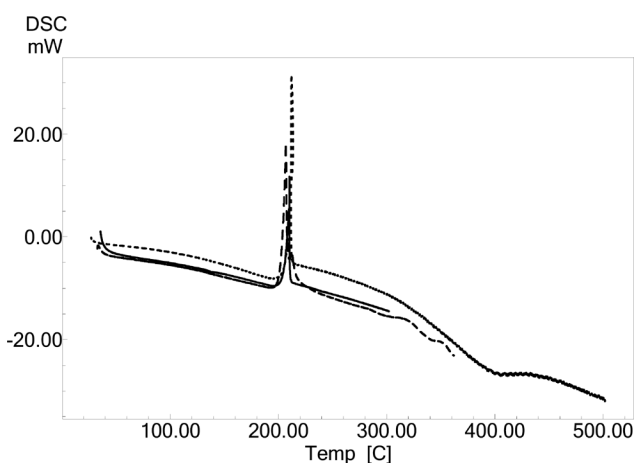
Mass losses in the first thermal reaction in the complexes containing nitrate ions are about 82 % for $\text{CuppNO}_3\text{N}_3 \cdot 2\text{H}_2\text{O}$ (**II**), and 30 % for $\text{CudmppNO}_3\text{N}_3 \cdot \text{H}_2\text{O}$ (**V**). Mass loss for $\text{CumppNO}_3\text{N}_3$ (**VIII**), however, is about 91 %. In this group, order of the amount of exothermal temperatures is:

$\text{CudmppNO}_3\text{N}_3 \cdot \text{H}_2\text{O}$ (**V**) > $\text{CuppNO}_3\text{N}_3 \cdot 2\text{H}_2\text{O}$ (**II**) > $\text{CumppNO}_3\text{N}_3$ (**VIII**).

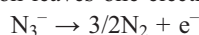
What is abnormal here is the 30 % mass loss observed in the first thermal decomposition of the $\text{CudmppNO}_3\text{N}_3 \cdot \text{H}_2\text{O}$ (**IV**) complex. As can be seen in the TG curve of this complex, there is a two step exothermic decomposition between $220\text{--}260^\circ\text{C}$. The experimentally found mass ratio of the azide group is 29.60 %, on the other hand the theoretically expected value is 9.28 %. It is more likely than not that this two step decomposi-

Table 4. Thermoanalytical data of the complexes.

Complex	First thermal reaction – removal of crystalline water			Second thermal reaction – decomposition of azide ions			Third thermal reaction – decomposition of residue		
	Temperature range /°C	Calculated mass loss /%	Experimental mass loss /%	Temperature range /°C	Calculated mass loss /%	Experimental mass loss /%	Temperature range /°C	Experimental mass loss /%	Measured energy by DSC /kJ·mol ⁻¹
I	–	–	–	213–222 DTG: 219	11.93	82.50 ± 2.65	–	–	133.35 ± 1.16
II	43–74	8.68	8.50	223–254	10.12	81.90 ± 1.86	255–306	Combining with first reaction	327.88 ± 12.11
III	78–110	Total	–	DTG: 248 191–205 DTG: 202	23.44	94.50 ± 2.68	DTG: 269	–	459.52 ± 16.45
IV	–	–	–	204–213 DTG: 209	10.28	84.80 ± 1.22	–	–	221.94 ± 10.77
V	60–76 DTG: 68	3.97	3.72	220–260 DTG: 234–251	9.28	29.60 ± 1.44	414–478	47.15 ± 1.24	346.71 ± 12.07
VI	–	–	–	Two steps 193–207 DTG: 205	20.25	95.84 ± 1.38	–	–	439.90 ± 14.96
VII	–	–	–	199–208 DTG: 206	11.04	91.25 ± 1.78	–	–	157.60 ± 7.24
VIII	–	–	–	195–209 DTG: 204	10.33	91.66 ± 4.70	–	–	240.64 ± 6.87
IX	–	–	–	214–224 DTG: 220	21.71	92.22 ± 3.18	–	–	411.28 ± 27.48

**Figure 6.** TG curves of Cupp(N₃)₂ —, Cu mpp(N₃)₂ ·····, Cu dmpp(N₃)₂ ----.**Figure 7.** DSC curves of Cupp(N₃)₂ —, Cu mpp(N₃)₂ ·····, Cu dmpp(N₃)₂ ----.

tion accounts for the thermal decomposition of the azide group together with its distributing its energy to the whole molecule causing some of the molecules exothermally decompose as whole. But not all of the molecules decomposed since the azide ion leaves one electron during the decomposition:



This electron is capable of turning Cu²⁺ ion into Cu⁺ and so, CudmppNO₃ may be formed. There are examples of such Cu^I complexes in the literature.^[4, 26] It is thought that a second thermal decomposition occurs with the oxidizing effect of the nitrate in CuppNO₃N₃ (**II**) and CumpNO₃N₃ (**VIII**) complexes following the breaking of the azide group. However, there is a temperature difference of 100 °C between the two reactions of the CudmppNO₃N₃ (**V**) complex. This difference was thought to be an experimental error, but then the experiment was repeated several times and the same result was ensured. However, a strong exothermal decomposition is also observed in this complex at around 400 °C (Figure 3). This decomposition is because of the oxidizing effect of the nitrate group. On the other hand, this cannot be seen in pp and mpp complexes, which decompose at about 200 °C with a mass loss of about 84–91 %, similar to those having one chlorine atom and one azide group. Probably, the energy arising from the exothermal decomposition of the azide is transferred to the molecule in these complexes, which leads to the decomposition of the whole molecule. Why the decomposition of the CudmppNO₃N₃ (**V**) complex doesn't resemble the decompositions of the CuppNO₃N₃ (**II**) and CumpNO₃N₃ (**VIII**) complexes? This question can be answered as the ligand is more electron donating. The reason for this electron donating behavior is the activation of the pyrazole rings by the four methyl groups. The more stable the Cu^IdmppNO₃ complex (the formation of which we assume) is, the more complex is left behind, and the carbonaceous remains decompose a second time with an intense exothermal reaction at around 400 °C. The methyl groups are electron donating and for this reason, the CudmppNO₃ complex, which is formed while the azide group

is decomposing, is of greater stability in $\text{CudmppNO}_3\text{N}_3$ (V) compared to the other two. However, this leaves another mystery behind. It does not explain why no similar happening occurs in CudmppClN_3 (IV).

All decompositions of the complexes with two azide groups are one-step decompositions with mass losses over 90 %. These compounds decomposed like energetic molecules, acting like alternative explosive material. The two azide groups are ruptured at around 200 °C transferring their energy to the remaining molecule, which then leads to the decomposition of the organic material exothermally and rapidly like explosive material (Figure 6 and Figure 7).

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