

Construction of Energetic Complexes Based on LLM-105 and Transition Metal Cations (Ni, Co, Mn, and Cu)

Yiyi Xiao ^{1,2}, Hui Huang ^{2,*}, Jinkun Guo ², Mi Yan ², Liyuan Wei ², Yu Liu ², Shiliang Huang ^{2,*}, Rufang Peng ¹ and Bo Jin ^{1,*}

¹ State Key Laboratory of Environment-Friendly Energy Materials, Southwest University of Science and Technology, Mianyang 621010, China; xiaoyiyihx@163.com (Y.X.); rfpeng2006@163.com (R.P.)

² Institute of Chemical Materials, China Academy of Engineering Physics (CAEP), Mianyang 621900, China; guojinkun22@gscaep.ac.cn (J.G.); yanmi_secret@163.com (M.Y.); weiliyuan21@gscaep.ac.cn (L.W.); liuyu307@caep.cn (Y.L.)

* Correspondence: huanghui@caep.cn (H.H.); shilianghuang@caep.cn (S.H.); jinbo0428@163.com (B.J.)

Abstract: Energetic complexes represent a crucial research direction for the design and synthesis of novel energetic materials. In this work, 2,6-diamino-3,5-dinitropyrazine-1-oxide (LLM-105), a significant explosive compound with exceptional comprehensive properties, was selected as the ligand for coordinating with various metal ions. Four novel energetic complexes, Ni(C₄H₃N₆O₅)₂·DMF (**1**), Co(C₄H₃N₆O₅)₂·2DMF (**2**), Mn(C₄H₃N₆O₅)₃·3/2DMF (**3**), and Cu₃(C₄H₂N₆O₅)₃·3DMF (**4**) were successfully synthesized, and their crystal structures were identified by a single-crystal X-ray diffraction technique. The structural analyses illustrated that LLM-105 can form either a mononuclear metal complex after the deprotonation of one amino group or a trinuclear metal complex after the deprotonation of two amino groups. Compound **1** exhibits a planar quadrilateral geometry, while both compounds **2** and **3** display distorted octahedral configurations. Compound **4** has three metal centers and exhibits two coordination configurations of distorted tetragonal pyramid geometry and planar quadrilateral geometry. The detonation performances of compounds **1**–**4** were also theoretically calculated, revealing their favorable explosive properties. These findings emphasize the diverse coordination modes of LLM-105 and the structural variability and adjustability of its complexes, offering valuable insights for regulating both the structure and performance of the LLM-105 complex as well as researching its deprotonation.

Keywords: energetic complexes; LLM-105 ligand; single-crystal structure; coordination modes



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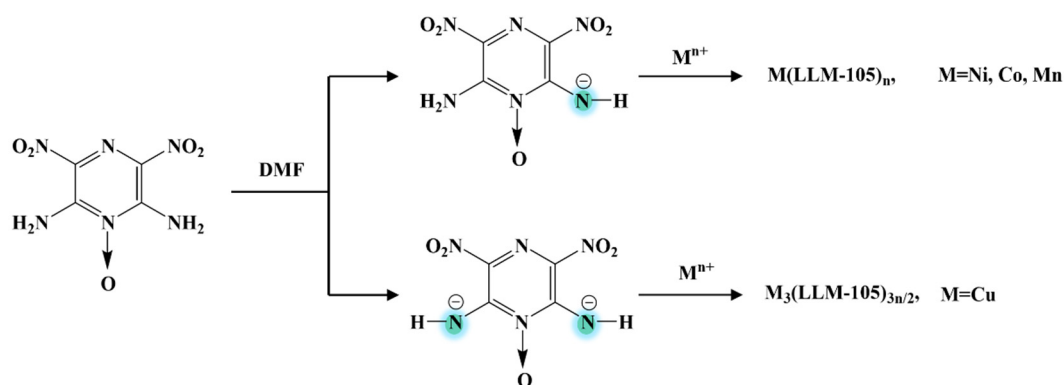
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1. Introduction

New energetic materials with high performance have been an urgent need in the military and aerospace industries [1–3]. Combining in-used energetic molecules with various metal cations to form energetic complexes is an important research direction in the design and synthesis of new energetic materials. Most studies have focused on compounds such as azide [4–6], hydrazine [7,8], triazole [9–11], and tetrazole [12,13], and their derivatives [14,15], due to their abundant coordination sites and high heat of formation which positively contribute to energy-level assurance. However, the properties of these ligands make it difficult for energetic complexes to meet both high energy and safety engineering requirements simultaneously. A typical example includes nickel hydrazine perchlorate (NHP) and cobalt hydrazine perchlorate (CHP), which possess detonation energies comparable to the two most commonly used organic explosives, pentaerythritol tetranitrate (PETN) and hexahydro-1, 3, 5-trinitro-1, 3, 5-triazine (RDX) [7]. Nevertheless, due to the low stability of perchlorate, the sensitivity of NHP and CHP remains exceptionally high, with NHP capable of detonating even in the absence of external stimuli, while CHP exhibits an impact sensitivity of 0.5 J or 20 cm (using a 2.5 kg weight). Therefore, the utilization

of high-energy and low-sensitivity energetic molecules as ligands is crucial in obtaining energetic complexes with exceptional comprehensive properties.

2,6-diamino-3,5-dinitropyrazine-1-oxide (LLM-105) has garnered significant attention for its high thermal stability and insensitivity to friction, shock, impact, and electrical spark [16–19]. As a result of these properties, it is considered as a promising alternative to 2, 4, 6-triamino-1, 3, 5-trinitrobenzene (TATB) for use as an insensitive detonator or main charge. As a polyamino-polynitro pyrazine nitrogen oxide, LLM-105 serves as an excellent example of a nitrogen-rich energetic ligand. However, due to the lack of knowledge regarding to coordination chemistry of LLM-105, it is still a big challenge to synthesize the metal complexes of LLM-105. To the best of our knowledge, only three complexes of LLM-105 with Cu(II), Co(III), and Pb(II) as the metal center have been synthesized so far [20,21]. In addition, the crystal structure of the Pb(II) complex of LLM-105 failed to be determined by a single-crystal X-ray diffraction technique (SCXRD). Here, the Co(II), Mn(III), and Ni(II) complexes of LLM-105 were first synthesized and confirmed by SCXRD. We also report another Cu(II) complex of LLM-105 with a coordination pattern that is completely different from the previously reported one. The synthesis route was illustrated in Scheme 1. These findings will markedly expand the coordination chemistry and potential applications of LLM-105.



Scheme 1. Reactions of LLM-105 with different metal ions in DMF.

2. Results and Discussion

2.1. Structures

Four metal complexes of LLM-105 were synthesized by adding LLM-105 to *N,N*-dimethylformamide (DMF) solutions of $Cu(NO_3)_2 \cdot 5H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$, and $MnCl_2$, respectively. After ultrasonic dissolution of the raw materials at 60 °C, the solution was allowed to stand at room temperature for one to two months until $Ni(C_4H_3N_6O_5)_2 \cdot DMF$ (**1**), $Co(C_4H_3N_6O_5)_2 \cdot 2DMF$ (**2**), $Mn(C_4H_3N_6O_5)_3 \cdot 3/2DMF$ (**3**), and $Cu_3(C_4H_2N_6O_5)_3 \cdot 3DMF$ (**4**) crystals were precipitate. The structures of these complexes were identified using a single-crystal X-ray diffraction diffractometer. Crystallographic data are summarized in Table 1. The bond lengths between non-hydrogen atoms are listed in Tables S1–S4 in the Supporting Information.

Compound **1** crystallizes in a monoclinic crystal system (space group $P21/c$). One amino group of the LLM-105 molecule is deprotonated and then coordinates to the Ni^{2+} ion, forming a square planar nickel complex by two N atoms and two O atoms, as shown in Figure 1. The nickel atoms are located on the center of inversion, with cis angles ($O1-Ni1-O6=90.62^\circ$; $O6-Ni1-N9=85.24^\circ$; $N9-Ni1-N3=99.19^\circ$; $N3-Ni1-O1=84.94^\circ$) and trans angles ($O1-Ni1-N9=175.85^\circ$; $O6-Ni1-N3=175.57^\circ$) showing a tetrahedral distortion. The bond lengths of $Ni1-N9$, $Ni1-O1$, $Ni1-N3$ and $Ni1-O6$ are 1.841(2), 1.843(2), 1.848(2), and 1.8625(19) Å, respectively. The C–N bond of the deprotonated amino group ($C4-N3=1.289(3)$ Å, $C6-N9=1.289(3)$ Å) is shorter than the C–N bond of the normal amino group ($C2-N4=1.310(3)$ Å, $C8-N10=1.324(4)$ Å) by about 0.03 Å, which agrees well with the

literature [22] and further confirms the deprotonation of LLM-105 during the formation of the metal complex.

Table 1. Crystallographic data of LLM-105-based metal complexes.

Compound	1	2	3	4
Formula	$C_{11}H_{13}N_{13}NiO_{11}$	$C_{14}H_{20}CoN_{14}O_{12}$	$C_{33}H_{39}Mn_2N_{39}O_{33}$	$C_{21}H_{25}Cu_3N_{21}O_{18}$
MW/(g/mol)	562.03	635.37	1619.91	1050.27
Crystal system	monoclinic	monoclinic	trigonal	monoclinic
Space group	$P 21/c$	$C 2/c$	$R \bar{3}$	$C 2/c$
$a/\text{\AA}$	15.2819(2)	16.80800(10)	15.7601(3)	19.7761(4)
$b/\text{\AA}$	13.0345(2)	6.999	15.7601(3)	19.5785(3)
$c/\text{\AA}$	9.9895(2)	20.96050(10)	24.0861(8)	9.6564(2)
$a/^\circ$	90	90	90	90
$b/^\circ$	92.204(2)	105.0760(10)	90	96.095(2)
$g/^\circ$	90	90	120	90
Cell vol / $\text{\AA}^3$	1988.36(6)	2380.91(2)	5181.0(3)	3717.69(12)
$r_{\text{calc}}/(\text{g}/\text{cm}^3)$	1.878	1.773	1.558	1.877
Z	4	4	3	4
Temperature/K	294	294	294	294
$F(000)$	1144	1300	2472	2116
$R_1 [I > 2s(I)]$	0.0469	0.0337	0.0748	0.0538
$wR_2 [I > 2s(I)]$	0.1444	0.0991	0.2363	0.1526
R_1 (all data)	0.0510	0.0358	0.0778	0.0643
wR_2 (all data)	0.1484	0.0998	0.2419	0.1613
GOF	1.074	1.090	1.092	1.055
CCDC number	2274630	2274631	2274633	2274632

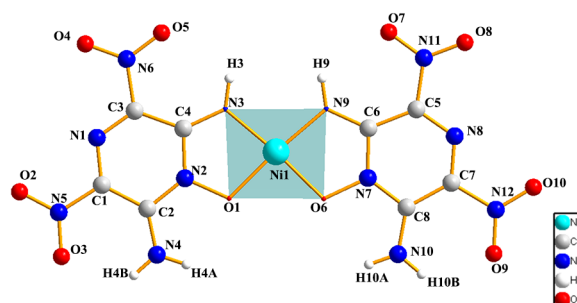


Figure 1. Coordination environment of compound 1.

Furthermore, due to the presence of abundant hydrogen bonds (Table S5), $N10-H10A \cdots O3$, $N4-H4A \cdots O2$, $N4-H4B \cdots O4$, $N9-H9 \cdots O11$, $N3-H3 \cdots O11$, and $C9-H91 \cdots O9$ hydrogen bonds, the nickel complex is linked into a molecular sheet, as shown in Figure 2a. Then, the formation of a three-dimensional (3D) supramolecular structure is facilitated by the π -stacking interactions, with a distance of 3.315 Å between the nitro group and the center of the pyrazine ring; electrostatic interactions, with a distance of 3.237 Å between the un-deprotonated amino groups and nickel ions; as well as weak hydrogen bonding ($C11-H11A \cdots O8$) between DMF and LLM-105, as depicted in Figure 2b–d.

Compound 2 crystallizes in a monoclinic crystal system (space group $C2/c$). The Co(II) ion is coordinated by two protonated LLM-105 and two DMF molecules, forming a slightly distorted octahedral geometry, as shown in Figure 3. The equatorial plane of the octahedron is defined by two oxygen atoms and two nitrogen atoms from two LLM-105 ligands with the $Co1-O1$ distance of 2.0413(12) Å, as well as $Co1-N4$ distance of 2.0968(18) Å. The axial position of the octahedron is occupied by two oxygen atoms from two DMF molecules with the $Co1-O6$ distance of 2.2084(14) Å. The shorter Co–O distance of LLM-105 anions indicates its stronger coordination interaction with the Co(II) ion than the DMF molecules.

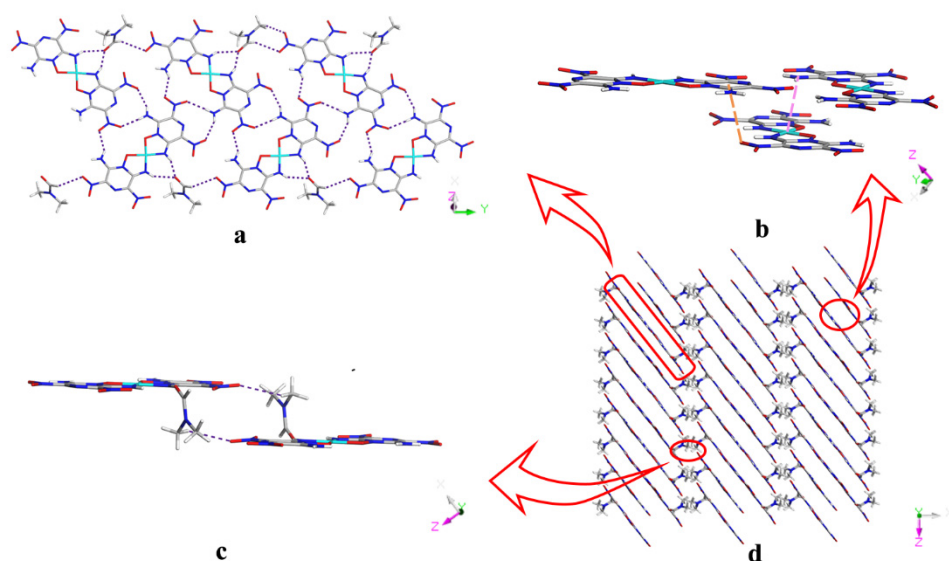


Figure 2. (a) Hydrogen bond modes leading to a sheet. (b) Electrostatic interaction (the pink dotted lines) and π -stacking modes (the orange dotted lines) leading to a 2D supermolecular layer. (c) Hydrogen bonds between layers. (d) The 3D supramolecular architecture of compound 1.

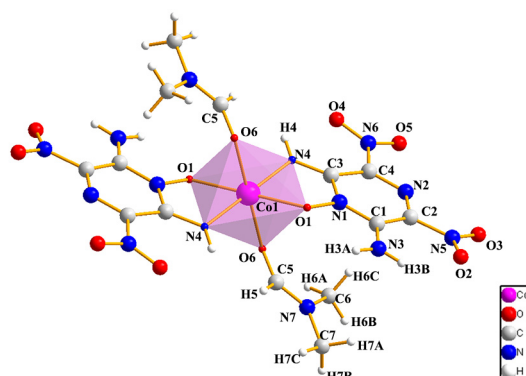


Figure 3. Coordination environment of compound 2.

The cobalt complex was linked into chains along the *b*-axis via multiple hydrogen bonds C6–H6A $\cdots$ O2, N3–H3B $\cdots$ O6, and N3–H3A $\cdots$ O1, as shown in Figure 4a and Table S6. Subsequently, a 3D supramolecular structure is generated through the intermolecular hydrogen bonds C7–H7C $\cdots$ O3 and C7–H7A $\cdots$ O3 between LLM-105 anions and the coordinated DMF molecules (Figure 4b,c).

Compound 3 crystallizes in the trigonal space group *R*-3. The LLM-105 molecules were also deprotonated, and each manganese atom is coordinated by three symmetrically related LLM-105 anions, forming a distorted octahedral geometry, as shown in Figure 5. Therefore, the three coordination bonds of Mn–N are symmetrically equal, with a bond length of 1.893(3) Å. The Mn–O bonds are in the same situation with a bond length of 1.906(2) Å. It is worth mentioning that the Mn(III) ion in the complex results from the oxidation of the Mn(II) ion in the raw material, MnCl₂, due to the variable valence state of Mn in solution [23–25]. This oxidation of Mn(II) can also be confirmed by the shorter Mn–N and Mn–O bonds in compound 3 compared to those in the other six-coordinated Mn(II) complexes in the literature [26–28], which is normally larger than 2.0 Å.

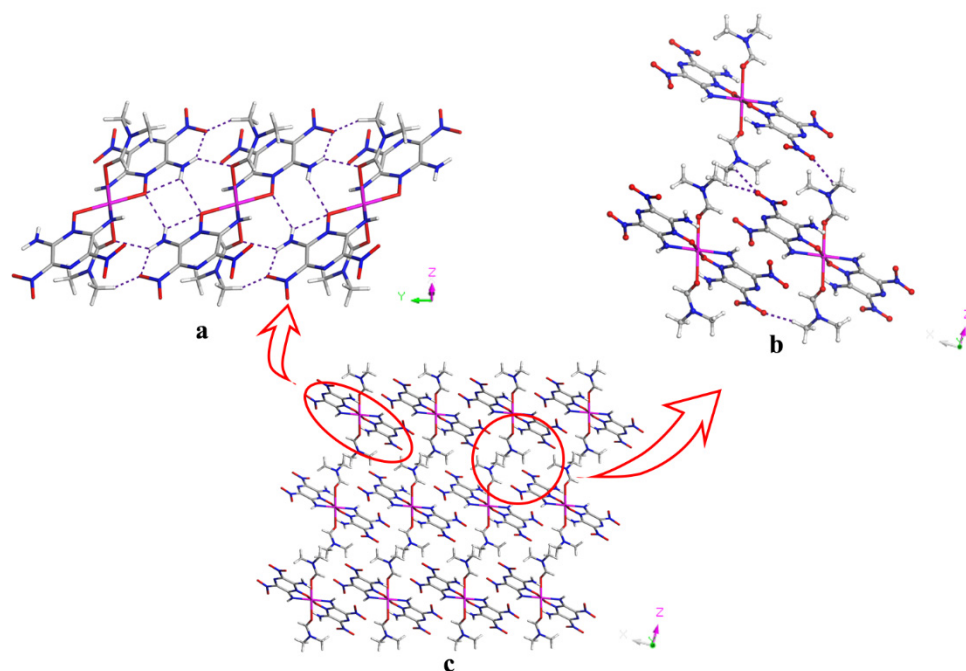


Figure 4. (a) Hydrogen bond modes leading to a chain along the y -axis. (b) Hydrogen bond modes leading to a 3D structure. (c) The 3D supramolecular architecture of compound 2.

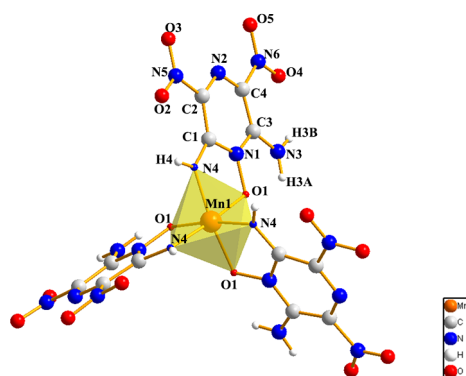


Figure 5. Coordination environment of compound 3.

These distorted octahedral complexes are further interconnected by hydrogen bonds $N3-H3B \cdots O2$ and $N3-H3B \cdots O3$ (Figure 6a and Table S7) to form a cavity structure, within which disordered DMF is fixed through hydrogen bonding $N3-H3A \cdots O6$ (Figure 6b) between its carbonyl group and the amino group of LLM-105, ultimately resulting in the formation of a three-dimensional structure (Figure 6c).

Compound 4 crystallizes in monoclinic space group $C2/c$. Unlike other LLM-105-based complexes, both amino groups of LLM-105 in 4 are deprotonated, enabling it to efficiently coordinate with copper ions as a tridentate ligand. Ultimately, complex 4 shows a trinuclear structure comprising three central Cu(II) ions, three LLM-105 anions, and two DMF molecules, as seen in Figure 7. Two of the copper atoms (Cu1) exhibit a five-coordinated configuration which are symmetrically related, while the remaining copper atom (Cu2) exhibits a four-coordinated configuration.

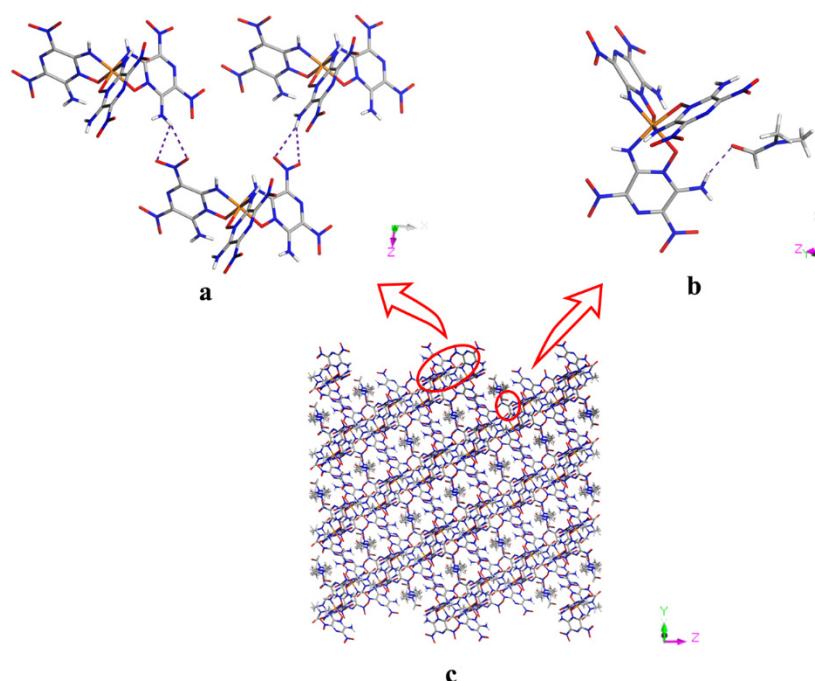


Figure 6. (a) Hydrogen bonds between the distorted octahedral motifs. (b) Hydrogen bonds between the DMF and distorted octahedral motif. (c) The 3D supramolecular architecture of compound 3.

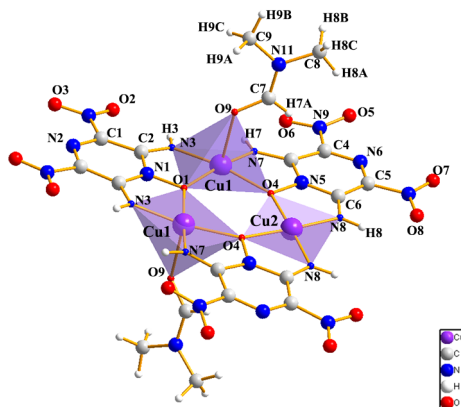


Figure 7. Coordination environment of compound 4.

The Cu1 atom is coordinated by two protonated LLM-105s and one DMF molecule, forming a distorted tetragonal pyramidal geometry, as depicted in Figure 7. The equatorial plane of the tetragonal pyramid is defined by two oxygen atoms and two nitrogen atoms from two LLM-105 ligands, with the Cu–O distances of 1.9960(12) Å (Cu1–O1) and 2.016(3) Å (Cu1–O4), as well as Cu–N distances of 1.920(3) Å (Cu1–N3) and 1.924(3) Å (Cu1–N7). The axial position of the tetragonal pyramid is occupied by one oxygen atom from a DMF molecule, with a Cu1–O9 distance of 2.353(3) Å. The shorter Cu–O and Cu–N distances of LLM-105 anions suggest that the coordination of LLM-105 with Cu1 is more robust than that of DMF with Cu1.

In contrast, the coordination environment around the Cu2 atom involves only two LLM-105 anions, forming a planar quadrilateral geometry, as illustrated in Figure 7. The bond lengths of Cu2–N8 and Cu2–O4 are 1.907(4) and 1.984(2) Å, respectively, which are significantly shorter than the coordination bond lengths of Cu1–N and Cu1–O, indicating a stronger binding force between Cu2 and LLM-105.

Furthermore, the copper complex is linked into chains along the *c*-axis through π -stacking interactions and electrostatic interactions (Figure 8a). Among them, the π -stacking

interactions are formed between the C3 atoms and the center of the pyrazine ring, with a distance of 3.276 Å (Figure S1). The electrostatic interactions primarily occur between the Cu1 and N3 atoms, as well as between the Cu2 and O2 atoms, at distances of 3.236 Å and 3.007 Å, respectively (Figures S2 and S3). Subsequently, these chains are further connected by the hydrogen bonds C8–H8C...O3 and C9–H9A...O7 between the coordinated DMF and LLM-105 anions to form a 3D structure with cavities, which are filled by disordered DMF molecules through hydrogen-bonding interactions between their carbonyl groups and the imino groups of LLM-105 (Figure 8b–d and Table S8).

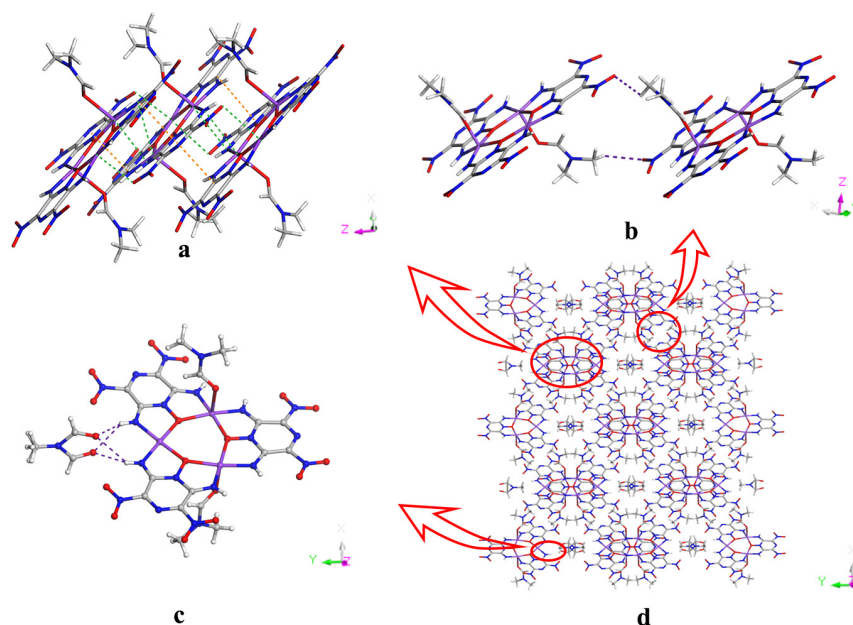


Figure 8. (a) Electrostatic interaction (the green dotted lines) and π -stacking (the orange dotted lines) modes leading to a chain along the z-axis. (b) Hydrogen bonds between the chains. (c) Hydrogen bonds between the disordered DMF and motif of compound **4**. (d) The 3D supramolecular architecture of compound **4**.

Compared with the previously reported tetranuclear Cu(II) complex based on LLM-105 [20], the structure in this work shows a new coordination mode, thereby highlighting the diverse coordination capabilities of LLM-105.

2.2. Energetic Properties

The detonation velocity and pressure are the primary parameters used to characterize the detonation properties of energetic materials [29]. Currently, the calculation of these parameters for energetic complexes primarily relies on the enhanced Kamlet–Jacob formula [30], as depicted in Equations (1)–(3):

$$D = 1.01\Phi^{\frac{1}{2}}(1 + 1.30\rho) \quad (1)$$

$$P = 1.558\Phi\rho^2 \quad (2)$$

$$\Phi = 31.68N(MQ)^{1/2} \quad (3)$$

where D is the detonation velocity (km/s), P is the detonation pressure (GPa), N is the moles of detonation gases per gram of explosive, M is the average molecular weight of the gases, Q is the heat of detonation per gram of explosive (kcal/g^{−1}), and ρ is the density (g/cm³).

To evaluate the heat of detonation (ΔH_{det}), density functional theory (DFT) is used to determine the explosion energy of detonation (ΔE_{det}), from which ΔH_{det} is estimated by

using a linear correlation equation ($\Delta H_{\text{det}} = 1.127\Delta E_{\text{det}} + 0.046$, $r = 0.968$) [7,8]. The DFT calculation is performed using the DMOL3 module within the Materials Studio software, and the results are shown in Table 2. For all the complexes, **1**, **2**, **3**, and **4**, water, carbon dioxide, carbon, and nitrogen were assumed to be the final products of decomposition of the organic components, and the formation of metal oxide was assumed to be governed by the content of oxygen. In addition to metal oxides and carbon, the rest of the final products are considered as the gas phase. The complete detonation reactions of **1**, **2**, **3**, and **4** are described by Equations (4)–(7):

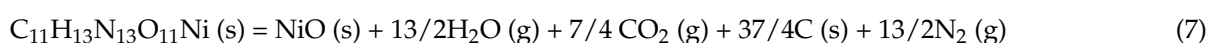
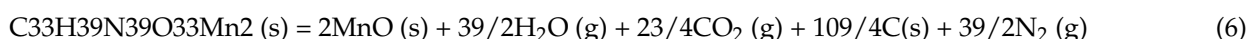
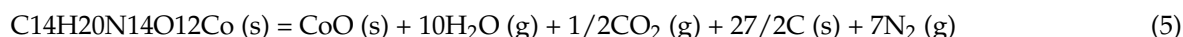
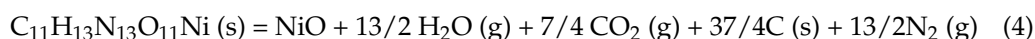


Table 2. Calculated parameters used in the detonation reactions.

	1	2	3	4
Complex/hartree	−2158.31	−2380.3	−6845.13	−4059.35
NiO (s)/hartree	−268.57			
CoO (s)/hartree		−241.89		
MnO (s)/hartree			−196.91	
CuO (s)/hartree				−272.48
H ₂ O (g)/hartree	−76.38	−76.38	−76.38	−76.38
CO ₂ (g)/hartree	−188.18	−188.18	−188.18	−188.18
C (s)/hartree	−37.74	−37.74	−37.74	−37.74
N ₂ (g)/hartree	−109.45	−109.45	−109.45	−109.45
ΔE_{det} /hartree	3.44	4.61	717.18	157.34
ΔE_{det} /(kcal/g)	3.84	4.55	277.78	93.99
ΔH_{det} /(kcal/g)	4.37	5.17	313.09	105.98

By substituting the calculated values of heat of detonation into Equation (3), the Φ values for complexes **1**, **2**, **3**, and **4** are determined to be 8.78, 9.47, 78.50, and 36.63 respectively. Subsequently, by plugging these values into Equations (1) and (2), the detonation velocities for the four complexes are found to be 10.29, 10.27, 27.07 km/s, and 18.49 km/s, respectively; while the detonation pressures are measured at 48.24, 46.36, 296.88 GPa, and 138.55 GPa, respectively. It should be noted that due to the presence of metallic elements, the calculated results may be slightly overestimated. In our future work, we will continue to optimize the synthesis conditions and improve yields to complete relevant performance testing. However, these results, to some extent, reflect the energy characteristics of these complexes.

3. Conclusions

In summary, the utilization of LLM-105 as ligands has led to the successful synthesis of four novel energetic complexes, which have been thoroughly characterized through single-crystal X-ray diffraction analysis. It was illustrated that LLM-105 can form either a mononuclear metal complex after the deprotonation of one amino group, or a trinuclear metal complex after the deprotonation of two amino groups. The mononuclear metal complexes of LLM-105 include Ni(C₄H₃N₆O₅)₂·DMF (**1**), Co(C₄H₃N₆O₅)₂·2DMF (**2**), and Mn(C₄H₃N₆O₅)₃·3/2DMF (**3**). In their structures, LLM-105 acts as a bidentate ligand, coordinating with the metal center atom through one oxygen atom and one nitrogen atom, forming either a planar square or a distorted octahedral configuration. The trinuclear complex of LLM-105 is Cu₃(C₄H₂N₆O₅)₃·3DMF. In this structure, LLM-105 serves as a tridentate ligand, coordinating with three metal center atoms while exhibiting both planar square geometry and tetragonal pyramidal geometry. In addition, the detonation

performances of compounds 1–4 were also theoretically calculated, revealing their favorable explosive properties. These results show that LLM-105 has abundant coordination modes, which makes the LLM-105 complex have structural diversity and adjustability, providing valuable insights for regulating both the structure and performance of the LLM-105 complex as well as researching its deprotonation.

4. Experimental Section

4.1. Caution

Although we experienced no difficulties in the synthesis and characterization of these materials, small-scale syntheses are strongly encouraged. All the compounds should be handled with extreme care by using the best safety practices.

4.2. Materials

LLM-105 was supplied by the Institute of Chemical Materials, China Academy of Engineering Physics (CAEP). $\text{Cu}(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, MnCl_2 , and DMF were purchased from Aladdin (Shanghai, China). All the chemical reagents and solvents were used as supplied without further purification.

4.3. Synthesis of $\text{Ni}(\text{LLM-105})_2 \cdot \text{DMF}$ (1)

To 5 mL of DMF, 0.03 g of LLM-105 and 0.25 g of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were added, followed by ultrasound treatment at 60 °C. Upon achieving solution transparency, the glass vial was sealed with a plastic film containing small perforations and left at ambient temperature for crystallization to occur, resulting in the formation of several dozens of crimson crystals identified as compound 1.

4.4. Synthesis of $\text{Co}(\text{LLM-105})_2 \cdot 2\text{DMF}$ (2)

To 5 mL of DMF, 0.03 g of LLM-105 and 2.50 g of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ were added, followed by ultrasound treatment at 60 °C. Upon achieving solution transparency, the glass beaker was sealed with a plastic film containing small perforations and left at ambient temperature for crystallization to occur, resulting in the formation of several dozens of brown crystals identified as compound 2.

4.5. Synthesis of $\text{Mn}(\text{LLM-105})_3 \cdot 3/2\text{DMF}$ (3)

To 5 mL of DMF, 0.03 g of LLM-105 and 0.25 g of MnCl_2 were added, followed by ultrasound treatment at 60 °C. Upon achieving solution transparency, the glass vial was sealed with a plastic film containing small perforations and left at ambient temperature for crystallization to occur, resulting in the formation of several dozens of black crystals identified as compound 3.

4.6. Synthesis of $\text{Cu}_3(\text{LLM-105})_3 \cdot 3\text{DMF}$ (4)

To 5 mL of DMF, 0.03 g of LLM-105 and 0.25 g of $\text{Cu}(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$ were added, followed by ultrasound treatment at 60 °C. Upon achieving solution transparency, the glass vial was sealed with a plastic film containing small perforations and left at ambient temperature for crystallization to occur, resulting in the formation of several dozens of brown crystals identified as compound 4.

4.7. Structure Determination

Single-crystal X-ray diffraction data of LLM-105-based complexes were collected on XtaLAB diffractometer with $\text{Cu-K}\alpha$ ($\lambda = 1.54178 \text{ \AA}$) radiation. The data were processed using CrysAlisPro (Rigaku Oxford Diffraction) and were absorption-corrected. The structures were determined and refined by SHELX. All non-hydrogen atoms were refined anisotropically, while the hydrogen atoms were located by geometrical calculations. It is worth mentioning that the DMF molecule in compound 3 has two disordered conformations. The

crystallographic information files (CCDC codes: 2274630–2274633) of the structures in this work can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/cryst13111587/s1>, Table S1: Bond lengths between non-hydrogen atoms in compound **1**; Table S2: Bond lengths between non-hydrogen atoms in compound **2**; Table S3: Bond lengths between non-hydrogen atoms in compound **3**; Table S4: Bond lengths between non-hydrogen atoms in compound **4**; Table S5: Geometric parameters of hydrogen bond interactions in compound **1**; Table S6: Geometric parameters of hydrogen bond interactions in compound **2**; Table S7: Geometric parameters of hydrogen bond interactions in compound **3**; Table S8: Geometric parameters of hydrogen bond interactions in compound **4**; Table S9: Geometric parameters of stacking interactions in compounds **1** and **4**; Figure S1: The π -stacking interactions between C3 atoms and pyrazine rings; Figure S2: The electrostatic interactions between Cu1 atoms and N3 atoms.

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