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A Carbon-free Inorganic-metal Complex Consisting of All-nitrogen Pentazole Anion, Zn(II) Cation and H₂O

A carbon-free inorganic-metal complex [7n/H-0].(N-1)./H-0 was synthesized by

Yuangang Xu, Pengcheng Wang,* Qiuhan Lin and Ming Lu*

A carbon-free inorganic-metal complex $[Zn(H_2O)_4(N_5)_2]$ ·4H₂O was synthesized by ion metathesis of $[Na(H_2O)(N_5)]$ ·2H₂O solution with $Zn(NO_3)_2$ ·6H₂O. The complex was well characterized by IR and Raman spectroscopy, elemental analysis (EA), powder X-ray diffraction (PXRD), and differential scanning calorimetry (DSC). The structure of the complex was confirmed by single-crystal X-ray crystallography and Zn(II) ion is coordinated in a quadrilateral bipyramid environment in which the axial position is formed by two nitrogen atoms (N1) from two pentazolate rings (*cyclo*-N₅⁻), the equatorial plane is formed by four oxygen atoms (O1) from four coordinated water molecules. Thermal analysis of $[Zn(H_2O)_4(N_5)_2]$ ·4H₂O reveal that although water plays an important role in stabilizing the *cyclo*-N₅⁻, dehydration does not cause immediate decomposition of the anion. However, *cyclo*-N₅⁻ decomposed into N₃⁻ and N₂ gas at 107.9 °C (onset). Based on its chemical compatibility and stability, the complex exhibit promising potential as modern environmentally-friendly energetic materials.

Introduction

The design of new high-energy density materials (HEDMs), encompassing all of propellants, explosives, and pyrotechnics, is a long-standing tradition in the chemical sciences.¹ In recent years, high nitrogen content materials have received copious attention due to their chemical interest and potential as HEDMs that are environmentally friendly (Fig. 1).²

It has been proposed that molecules containing nitrogen atoms connected by unstable single or double bonds decompose to give very stable N_2 molecules, along with the release of large amounts of energy³. From an alternative perspective, fully nitrogenated species are promising candidates as potential HEDMs, provided they are metastable. The well-established existence of azide-metal salts $(M(N_3)_n)^4$, and the recently reported N_5^+ salts⁵, demonstrate that allnitrogen compounds can be synthesized. Consequently, the development of all-nitrogen species is a challenging, but very attractive, objective for both industrial and academic purposes.

After the pioneering work of Huisgen and Ugi⁶ in the late 1950s, numerous attempts have been made to cleave the C-N bond of these aryl pentazoles and prepare the *cyclo*-pentazole anion (*cyclo*- N_5^-). The *cyclo*- N_5^- has attracted special attention since it was observed in the gas phase⁷ by collosion induced dissociation of *p*-oxidophenyl pentazole and then by laser desorption ionization of *p*-dimethylaminophenyl pentazole.

the same result in condensed phase by oxidative, reductive, and photo- cleavage methods had failed.⁸⁻¹¹ Until recently, a major push to these experiments was made when *cyclo*-N₅⁻ was prepared in the bulk. Bazanov *et al.*¹² found the evidence for the formation and direct detection of *cyclo*-N₅⁻ in THF solution. Zhang *et al.*¹³ end the long search for a bulk synthesis of the *cyclo*-N₅⁻. This anion was synthesized by oxidative cleavage of 3,5-dimethyl-4-hydroxyphenyl pentazole and characterized as a component in a solid salt (N₅)₆(H₃O)₃(NH₄)₄Cl.

After a long period of time, a variety of attempts to achieve



Fig. 1 Selected nitrogen-rich molecules.

Lein *et al.*¹⁴ pointed out that metals can stabilize *cyclo*-N₅^{\cdot}. Significant interests have been shown in finding suitable metal cations at theoretical level and their assembly into metal complexes¹⁵ have been investigated. These studies showed that *cyclo*-N₅^{\cdot} salts have high kinetic stability and high energy

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⁺ Electronic Supplementary Information (ESI) available: Experimental procedures and characterisation data for all compounds are provided. CCDC 1544795. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x

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content, which means that metal complexes of *cyclo*-N₅⁻ have immense potentials as HEDMs¹⁶. Recently, our group has been reported a series of metal-pentazole complexes¹⁷, including $[Na(H_2O)(N_5)]\cdot 2H_2O$, $[M(H_2O)_4(N_5)_2]\cdot 4H_2O$ (M = Mn, Fe, and Co), and $[Mg(H_2O)_6(N_5)_2]\cdot 4H_2O$, through ion metathesis of a N₅⁻ solution with either nitrate or chloride metal salts. $[Co(H_2O)_4(N_5)_2]\cdot 4H_2O$ was also synthesized through salt metathesis by reacting $(N_5)_6(H_3O)_3(NH_4)_4CI$ with $Co(NO_3)_2\cdot 6H_2O$.¹⁸

As we all know, the complexation ability of Zn to form complexes is much lower than Mn, Fe, and Co. So the synthesis of N₅-Zn complex is a great challenge. In the continuation of our efforts to search for a wide variety of metal N₅⁻ complexes, we find that Zn^{2+} cation can stabilize *cyclo*-N₅⁻ with the assistance of H₂O. With this strategy in mind, we describe herein the synthesis and characterization of $[Zn(H_2O)_4(N_5)_2]\cdot 4H_2O$ (**2**).

Results and discussion

Synthetic procedures

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As shown in Scheme 1, crystals **2** were formed *via* metathesis reactions between $[Na(H_2O)(N_5)]\cdot 2H_2O$ (1) and $Zn(NO_3)_2\cdot 6H_2O$ in 95% ethanol, recrystallization in anhydrous ethanol, followed by slow volatilization at room temperature. Unlike the previously reported method¹⁷, the preparation process adds a recrystallization step to reduce impurities that are not favorable for the formation of single crystals.

 $[Na(H_2O)(N_5)] \cdot 2H_2O \xrightarrow{Zn(NO_3)_2 \cdot 6H_2O} [Zn(H_2O)_4(N_5)_2] \cdot 4H_2O$ 95% EtOH

Scheme 1. Synthetic route to $[Zn(H_2O)_4(N_5)_2] \cdot 4H_2O$.

Crystal structure

Low-temperature single-crystal X-ray diffraction was used to characterize **2**. The detailed information including bond lengths, bond angles, and hydrogen bonds are given in the Supporting Information (Table S1-S3).

Zinc complex 2 crystallizes in the orthorhombic space group \textit{F}_{mmm} and a density of 1.669 g cm $^{-3}$ at 205 K (Table 1). The molecule, shown in Fig. 2, similar to we previously synthesized N₅-transition metal complexes $[M(H_2O)_4(N_5)_2] \cdot 4H_2O$ (M = Mn, Fe, and Co)¹⁷ pentagonal N₅⁻ exists a perfectly planar arrangement (N1-N2-N3-N3^{vii} 0°, N1-N2^{vii}-N3^{vii}-N3 0°) (Supporting Information, Fig. S1). The N-N bonds in the N₅ rings of different complexes are not of equal length, the average N-N bond distance in 2 is 1.328 Å, similar to $[Fe(H_2O)_4(N_5)_2]$ ·4H₂O (1.329 Å) and slightly longer than that of **1**, $[Mn(H_2O)_4(N_5)_2] \cdot 4H_2O$, and $[Co(H_2O)_4(N_5)_2] \cdot 4H_2O$ (1.316, 1.320, and 1.314 Å). Each Zn(II) ion (sp^3d^2) hybridization), contributes six empty orbits to accommodate the long pair electrons from ligands, is coordinated in a quadrilateral bipyramid environment in which the axial position is formed by two N1 atoms from two cyclo-N5⁻ rings, the equatorial plane

is formed by four O1 atoms from four coordinated water molecules (Zn1-O1 = 2.105 Å). The zinc atoms and the adjacent N₅ rings are also perfectly coplanar, which can be seen from the 180° (Zn-N1-N2-N3) torsion angle. The Zn1-N1 bond length in **2** is 2.155 Å, which is in agreement with the metal-nitrogen distance of 2.103 Å in Zn(5-NATZ)₂(H₂O)₄,¹⁹ while slightly longer than Co-N bond in [Co(H₂O)₄(N₅)₂]·4H₂O (2.122 Å) and obviously shorter than Fe-N bond in [Fe(H₂O)₄(N₅)₂]·4H₂O (2.257 Å).

The powder X-ray diffraction (PXRD) pattern of **2** is consistent with the simulated data for **2** (Fig. S4). From $[Mn(H_2O)_4(N_5)_2]\cdot 4H_2O$ to $[Fe(H_2O)_4(N_5)_2]\cdot 4H_2O$ to $[Co(H_2O)_4(N_5)_2]\cdot 4H_2O$, the main peaks shift slightly to a higher degree. Compared with $[Co(H_2O)_4(N_5)_2]\cdot 4H_2O$, the main peaks of **2** shift slightly to a lower degree indicating that the main frameworks of **2** and $[M(H_2O)_4(N_5)_2]\cdot 4H_2O$ (M = Mn, Fe, and Co) should remain consistent with each other.

Considering the stability of $(N_5)_6(H_3O)_3(NH_4)_4Cl^{13}$ and all the metal-N₅ complexes^{17,18}, it is important to note that, H_2O participates in the coordination process by forming new orbitals with both the metal and N_5^- (Fig. 3). Two forms of H_2O (constitution water H_2O (O2) and coordinated water H_2O (O1)) play a critical role in forming framework of hydrogen-bonding pairs.²⁰ As can be seen, the water molecule is not only a hydrogen-bond acceptor but also a hydrogen-bond donor. Each constitution water molecule (H₂O, O2) can participate in three different kinds of hydrogen-bond pairings, that is, sharing its two hydrogen atoms with two neighboring nitrogen atoms from two cyclo-N5⁻ rings (O2-H2a...N2, O2-H2b...N3) (Fig. 4a), and accepting one further hydrogen atom associated with a oxygen atom (O1-H1a...O2) (Fig. 4b). These hydrogenbonding pairs (O2 as donor) and coordination bonds (Zn1-N1) lead to a stable planar structure (Fig. S2). Abundant hydrogen bonds (O1-H1a...O2, O1-H1b...O1) between two forms of H₂O molecules (Fig. 4b) make the adjacent layers stack in sequence to become the stable 3D network (Fig. 4c and Fig. S3) and make an important contribution to enhance the thermal stability of the complex.



Fig. 2 Molecular structure of **2**. Ellipsoids represent the 50% probability level. Hydrogen bonds are marked as dashed lines.

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Fig. 3 Molecule orbital (MO) correlation diagrams for interactions between Zn^{2+} and N_5^- ligand with (b) and without (a) coordinated waters in complex 2.

Spectroscopic data

IR and Raman vibrational spectra of complex 2 are provided in Fig. 5 for further structural information. According to the references (ref. 13 and 18), cyclo- N_5 in $(N_5)_6(H_3O)_3(NH_4)_4Cl$ and $Co(N_5)_2(H_2O)_4 \cdot 4H_2O$ was considered to be D_{5h} symmetry. We put forward a completely different opinion here. After its coordination with a metal cation (Mn, Fe, Co, or Zn), cyclo-N₅ could not maintain the D_{5h} symmetry ($A_1' + E_1' + 2E_2' + E_2''$) but the C_{2v} symmetry $(A_1 + (A_1 + B_2) + 2(A_1 + B_2) + (A_2 + B_1))$ which could be conclude from the geometry structure of cyclo-N₅ according to the single-crystal X-ray diffraction. The $(A_2 + B_1)$ modes derived from E_2 " are neither infrared (IR)-active nor Raman-active. The $(A_1 + B_2)$ modes derived from E_1' are IRactive while the A_1 and $2(A_1 + B_2)$ modes evolved from A_1' and $2E_2'$ are Raman-active. Two cyclo-N₅⁻ bands at 1238 (A₁) and 1258 cm⁻¹ (B₂) are in excellent agreement with the frequencies observed in $[Na(H_2O)(N_5)] \cdot 2H_2O$, $[M(H_2O)_4(N_5)_2] \cdot 4H_2O$ (M = Mn, Fe, and Co), $[Mg(H_2O)_6(N_5)_2] \cdot 4H_2O$ and the theoretical frequency for these modes²¹. From $[Mn(H_2O)_4(N_5)_2] \cdot 4H_2O$ to $[Fe(H_2O)_4(N_5)_2] \cdot 4H_2O$ $[Co(H_2O)_4(N_5)_2] \cdot 4H_2O$ to to $[Zn(H_2O)_4(N_5)_2] \cdot 4H_2O$, the vibration wavenumbers of cyclo-N₅ increase gradually (A₁: 1232, 1232, 1236, 1238 cm⁻¹; B₂: 1252, 1255, 1256, 1258 cm⁻¹). The Raman spectrum of the investigated cyclo-N₅ exhibits a strong band for the A₁ mode at

1064 cm⁻¹ and the much weaker bands of $2(A_1 + B_2)$ modes at 721 and 1382 cm⁻¹.

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Fig. 4 (a) 2D layered intermolecular interactions in the crystal structure of complex **2**. (coordinated waters are omitted for clarity) (b) Hydrogen bonds between $cyclo-N_5^-$ planes. (c) 3D structural network in complex **2**.

	2
CCDC	1544795
Chemical formula	$H_{16}N_{10}O_8Zn$
Formula weight / g mol ⁻¹	349.60
Temperature / K	205
Wavelength / Å	0.71073
Crystal system	orthorhombic
Space group	<i>F</i> mmm
Crystal colour	colorless
Crystal size / mm ³	0.35×0.2×0.15
a / Å	12.293(4)
<i>b</i> / Å	17.319(6)
<i>c /</i> Å	6.536(2)
α / °	90
6 / °	90
γ/°	90
Volume / Å ³	1391.5(9)
Z	4
D_{calc} / g cm ⁻³	1.669
Absorption coefficient / mm ⁻¹	1.818
F(000)	720

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		Journal Name
ϑ range / $^{\circ}$	3.315-27.257	4
	-15 ≤ h ≤ 15,	^ exo
Index ranges	-21 ≤ k ≤ 22,	- <u>-</u> 111.7 °C
	-8 ≤ l ≤ 8	Ê 197.6 °C
Reflections collected	2971	\geq 0 \downarrow \checkmark \ast 266.0 °C
Goodness-of-fit on F^2	1.198	E V
R indices (all data)	$R_1 = 0.0303,$	<u>0</u> -2 52 1°C
	wR ₂ =0.0707	
Final <i>R</i> indices $[I>2\sigma(I)]$	$R_1 = 0.0302,$	-4 -
	wR ₂ =0.0707	
Largest diff. peak and hole / e Å ⁻³	0.48, -0.87	50 100 150 200 250 300 350 400 450 500
		Temperature (°C)

Fig. 6 DSC curve of **2** with a heating rate of 5 K min⁻¹.

Differential scanning calorimetry

The thermal stability of complex 2 was determined by differential scanning calorimetry (DSC) at 5 K min⁻¹ using dry nitrogen at 50 ml min⁻¹. About 0.6 mg sample was placed in perforated stainless steel containers. As can be seen in Fig. 6, complex 2 contains water moieties, only one endothermic process occurred at 27.4 °C (onset). It exhibited three exothermic stages. The first exothermic peak was similar to $[Mn(H_2O)_4(N_5)_2] \cdot 4H_2O$ (104.1 °C) that of and $[Fe(H_2O)_4(N_5)_2] \cdot 4H_2O (114.7 °C)^6$ occurring at 107.9 °C (onset) attributed to the decomposition of cyclo-N₅⁻ to N₃⁻ and N₂. The DSC reveals relatively good thermal stability for complex 2.

Moreover, from Fig. 6 we can see the exothermic heat from the decomposition of cyclo-N₅ to N₃ and N₂ at 111.7 °C (peak) is only one fifth of the endothermic heat from the water loss. In combination with previous studies, ^{13,17} We concluded that cyclo-N5 did not exist after 130 °C, azides continue to decompose at higher temperature. So we object to the "the pentazole-based metal species reported view $Co(N_5)_2(H_2O)_4 \cdot 4H_2O$ contains more energy and produced a stronger explosion than $(N_5)_6(H_3O)_3(NH_4)_4C{I''}^{18}$. The explosion is caused by the decomposition of cobalt azide (sensitive) instead of cyclo-N₅ (or Co(N₅)₂(H₂O)₄·4H₂O). The evaluation of the energetic performances of pentazole-based compounds requires more scientific and accurate criteria.



Wavenumbers (cm⁻¹)



Conclusions

In conclusion, we have synthesized a new stable metal-N₅ complex $[Zn(H_2O)_4(N_5)_2] \cdot 4H_2O$, assisted by H_2O . Unlike the previously reported D_{5h} symmetry, the single crystal structure of cyclo-N₅⁻ in this complex has C_{2v} symmetry. Zn(II) ion exhibits a slightly distorted octahedral configuration and the whole molecule is central symmetrical. Its abundant intermolecular hydrogen bonds make a vital contribution to the stable 3D structure ($T_{dec, onset}$ = 107.9 °C). On the basis of the compatibility between metals and cyclo-N5, HEDMs containing N_5 are expected to be realized in the near future.

Experimental section

Caution

Although we have not experienced any difficulties in synthesizing and handing the complex, it is a potentially dangerous explosive. Proper protective precautions (safety glasses, face shield, leather coat, earthen equipment and shoes, Kevlar gloves and ear plugs) must be used. All compounds should be stored in explosive cases as they can explode spontaneously.

General methods

All reagents and solvents were purchased from Sigma-Aldrich, Aladdin, and Energy Chemical as analytical grade and were used as received. DSC plots were acquired on a differential scanning calorimeter (Mettler Toledo DSC-1) at a scan rate of 5 °C min⁻¹ in perforated stainless steel containers under a nitrogen flow of 50 mL min⁻¹. IR spectra were recorded on a Thermo Nicolet IS10 instrument. Raman spectra were collected using a Horiba-Jobin Yvon Labram HR800 Raman spectrometer with a 514.532 nm Ar⁺ laser. A 50× objective was used to focus the laser beam. Elemental analyses were carried out on a vario EL III CHNOS elemental analyzer. Powder X-ray diffraction (PXRD) measurements were performed on a Bruker D8 Advance X-ray diffractometer using Cu K α (λ = 1.5406 Å) radiation.

X-ray crystallography

The single crystal X-ray diffraction measurements for 2 were conducted on a Bruker Smart Apex II diffractometer using Mo-Ka

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radiation (λ = 0.71073 Å) with a graphite monochromator at 205 K. An Oxford Cobra low-temperature device was used to maintain the low temperature. Integration and scaling of intensity data was accomplished using the SAINT program²². The structures were solved by intrinsic using SHELXT2014 and refinement was carried out by a full-matrix least-squares technique using SHELXT2014²³. The hydrogen atoms were refined isotropically, and the heavy atoms were refined anisotropically. N-H and O-H hydrogens were located from different electron density maps, and C-H hydrogens were placed in calculated positions and refined with a riding model. Data were corrected for the effects of absorption using SADABS²⁴.

Theoretical study

All computations were performed using the Gaussian 09 program²⁵ invoking hybrid HF-DFT calculations with the three-parameter gradient-corrected exchange potential of Becke and the gradientcorrected correlation potential of Lee, Yang, and Parr $(B3LYP)^{26}$. The elements H, N, and O were examined using the cc-pVTZ basis set. Transition metal Zn invoking effective core potentials (ECPs) on the heavier elements used the double- ζ valence basis set of Hay and Wadt, denoted as LANL2DZ²⁷. The structures were optimized for energy minimization before spectra acquisition and frequency calculations. The wave-functions of complexes generated from Gaussian were imported into the software Multiwfn²⁸ to perform Kohn-Sham orbitals prediction²⁹ and charge decomposition analysis (CDA).

Complex ${\bf 1}$ was prepared according to our previously reported methods. 17

[Zn(H₂O)₄(N₅)₂]·4H₂O (2): 1.0 mmol of [Na(H₂O)(N₅)]·2H₂O (147 mg) was added to 0.5 mmol Zn(NO₃)₂·6H₂O dissolved in 15 ml of ethanol (95%). The colorless solution was evaporated to dryness folloewd by repeated recrystallization in anhydrous ethanol to remove the sodium nitrate. Single crystal of [Zn(H₂O)₄(N₅)₂]·4H₂O (2) were obtained by maintaining 95% alcohol solutions at ambient temperature for several days. Colorless crystals; yield: 93%; $T_d = 107.9$ °C; IR (KBr): $\tilde{v} = 3346$, 3262, 1663, 1258, 1238, 570, 548 cm⁻¹; Raman (514.532 nm, 25 °C): 1382, 1064, 721, 180 cm⁻¹; Elemental analysis calcd (%) for H₁₆N₁₀O₈Zn (349.57): H 4.61, N 40.07; found: H 4.56, N 40.14.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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A carbon-free inorganic-metal complex $[Zn(H_2O)_4(N_5)_2] \cdot 4H_2O$ was synthesized by ion

metathesis of $[Na(H_2O)(N_5)]$ ·2H₂O solution with $Zn(NO_3)_2$ ·6H₂O in a perfect yield.