Crystal structure and solid-state properties of discrete hexa cationic trinuclear zinc triazole cluster

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Abstract. A linear trinuclear cluster of the type $[\{Zn_3(HTrz)_6(H_2O)_6\}^{6+}(NO_3^-)_6(H_2O)]$ (**ZnT**) has been synthesized by one-pot reaction between 1,2,4-triazole and $Zn(NO_3).6H_2O$. Molecule consists of three Zn^{2+} ions linearly connected by 1,2,4-triazole with tri-fold symmetry. The coordination geometry around the zinc centre is octahedral with zinc-zinc separation of 3.810 Å. The coordination environment of central Zn^{2+} ion is satisfied by nitrogen atoms of six 1,2,4-triazoles, while the geometry of terminal Zn^{2+} ions is fulfilled by nitrogen atoms of three 1,2,4-triazoles and three water molecules. The thermal and absorption properties of **ZnT** have been reported for the first time.

Keywords. Zinc; trizole; clusters; cationic compounds.

1. Introduction

The evolution of a new strategy for noetic design of poly-nuclear zinc clusters has led to special attention in supra-molecular chemistry.[1] The choice of multidentate ligands and zinc often leads to a well defined cluster with special properties.[2–4] For example, the zinc-rich clusters formed by binding of nitrogen donor in organic ligands are attractive building blocks to induce unusual thermal and optical properties to the materials.[5,6] These molecular assemblies often represent as models for the active sites of enzymes.[7] Controlling the nuclearity of zinc cluster complexes is one of the most challenging tasks, which may be solved using multidentate N-donor ligands.[1–4]

The multidentate N-donor ligands can be used in the construction of clusters or multi-dimensional coordination polymers. Of the many nitrogen-containing heterocycles, only the 1,2,4-triazole is particularly well established as being able to facilitate the formation of trinuclear complexes bridged by the adjacent nitrogen atoms.[8] Trinuclear complexes can be used as "cut out" of extended metal network to understand the magnetic and/or electrochemical behavior due to the synergism between metal centers. They can also be treated as bioinorganic models, to understand the mechanism of complex biological systems (e.g., metalloenzymes) or to reproduce their catalytic activity.[6,7]

For example, the first structurally characterized trinuclear complex $[Ni_3(Htrz)_6(H_2O)_6](NO_3)_6\cdot 2H_2O$ was reported by Reimann *et al*.[9] Subsequently several triazole bridged trinuclear clusters of Mn, Fe, Co and Ni were synthesized and structurally characterized.[8] However, similarity of molecular assembly of copper and zinc is very rare.[7] In particular, the triazole coordinated zinc assembly leads to the formation of insoluble coordination polymers. The only linear trinuclear zinc triazole assembly reported upto now is $[Zn_3(EtTrz)_6(H_2O)_6][CF_3SO_3]_6$ [**ZnT^E**], derived from 4-ethyl-1,2,4-triazole, where the zinc−zinc separation is 3.815 Å.[10] Of late, the $[Zn_3(HTrz)_6(H_2O)_6]^{6+}$ was isolated with decavanadate complex, $[V_{10}O_{28}]^{6+}$ as a counter ion in $[Zn_3(Htrz)_6(H_2O)_6]$ $[V_{10}O_{28}]\cdot 10H_2O\cdot Htrz$ (**ZnTV**) using 1,2,4-triazole, where the zinc−zinc separation is 3.805 Å.[11] Nevertheless, the strategies to isolate $[Zn_3(HTrz)_6(H_2O)_6]^{6+}$ from unsubstituted 1,2,4-triazole is not known. Thus, we report the synthesis, structural, optical and thermal properties of $[\{Zn_3(HTrz)_6(H_2O)_6\}^{6+}(NO_3^-)_6(H_2O)]$ (**ZnT**) obtained from the reaction between unsubstituted 1,2,4-triazole and $Zn(NO_3).6H_2O$.

2. Experimental

2.1 *General Procedures*

$Zn(NO_3)_2\cdot 6H_2O$ (Merck) and 1,2,4-triazole (Merck) were purchased from commercial sources. FT-IR measurement

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(neat) was carried out on a Bruker Alpha-P Fourier transform spectrometer. The thermogravimetric analysis (TGA) was performed using a TA-SDT Q600, Tzeropress. The UV−vis spectra were measured on a T90+ UV-visible spectrophotometer. Elemental analyses were performed by the Euro EA Elemental Analysis. The crystal structure of **ZnT** was measured on an Oxford Xcalibur 2 diffractometer with standard 4-circle kappa-goniometer, Eos detector (Active area 92 mm diagonal) and two X-ray sources one of which is Supernova Cu source (wave length 1.5418 Å) with focusing mirrors. A suitable crystal was selected and mounted on a Gemini E goniometer. Data were collected at 150 K using Oxford Cryojet Low-Temperature device. The structure of **ZnT** was solved by direct methods using the SIR-97 program[12] and refined with a full matrix least-squares method on F2 using the SHELXL-97 program.[13,14] No hydrogen atoms are given for a water molecule of O(13). Non-hydrogen atoms were anisotropically refined. H atoms were included in the refinement in calculated positions riding on their carrier atoms. No restraint has been made for any of the compounds. The function minimized was $[\sum w(F_o^2 - F_c^2)^2]$ (w = 1/$[\sigma^2(F_o^2) + (aP)2 + bP]$), where $P = (\max(F_o^2,0) + 2F_c^2)/3$ with $\sigma^2(F_o^2)$ from counting statistics. The functions R_1 and wR_2 were $(\sum||F_o| - |F_c||)/\sum|F_o|$ and $[\sum w(F_o^2 - F_c^2)^2/\sum(wF_o^4)]^{1/2}$, respectively. Crystallographic data for the structures are provided in tables 1–2. Structural diagrams were generated using the Diamond3.0 and Mercury3.1 program.

Table 1. Crystallographic data, details of data collection and structure refinement parameters for **ZnT**.

Empirical formula	$C_{12}H_{30}Zn_3N_{24}O_{26}$
Formula weight	1122.71
Temperature (K)	150(2)
Crystal system	Monoclinic
Space group	P2(1)/n
a, Å	13.153(3)
b, Å	11(2)
c, Å	14.333(3)
α,°	90
β,°	114.17(3)
γ,°	90
Volume, Å^3	2033.0(7)
Z	2
ρ_{calc}, mg mm^{-3}	1.834
μ, mm^{-1}	1.874
F(000)	1136
Data collected	7764
Unique data	3829
R_{int}	0.0251
GOF on F^2	1.077
R_1 ($I > 2\sigma(I)$)	0.0424
wR_2 ($I > 2\sigma(I)$)	0.1224

Table 2. Selected bond lengths [Å] and angles [°] of **ZnT**.

Bond lengths [Å]

N(1)–Zn(1)	2.126(3)	N(8)–Zn(1)	2.118(3)
N(3)–Zn(2)	2.189(3)	O(1)–Zn(1)	2.095(3)
N(4)–Zn(2)	2.155(3)	O(2)–Zn(1)	2.123(3)
N(5)–Zn(2)	2.176(3)	O(3)–Zn(1)	2.071(3)
N(6)–Zn(1)	2.143(3)		

Bond angles [deg]

O(3)–Zn(1)–O(1)	89.54(16)	N(8)–Zn(1)–N(6)	89.32(12)
O(3)–Zn(1)–O(2)	90.93(15)	O(1)–Zn(1)–N(6)	90.90(14)
O(1)–Zn(1)–O(2)	87.22(14)	N(8)–Zn(1)–N(1)	94.20(11)
O(3)–Zn(1)–N(8)	90.17(14)	N(1)–Zn(1)–N(6)	91.57(11)
N(8)–Zn(1)–O(2)	91.16(13)	N(4)–Zn(2)–N(5)	89.70(11)
O(3)–Zn(1)–N(1)	91.14(14)	N(4)–Zn(2)–N(3)	89.43(11)
O(1)–Zn(1)–N(1)	87.44(12)	N(5)–Zn(2)–N(3)	91.25(11)
O(2)–Zn(1)–N(6)	86.40(13)		

2.2 Synthesis of [{Zn_3(HTrz)_6(H_2O)_6}]^{6+}(NO_3^-)_6(H_2O)] (ZnT)

1,2,4-triazole (1.4 mmol) in MeOH/H$_2$O (1:1) was carefully layered on a solution of Zn(NO$_3$).6H$_2$O (0.7 mmol) in MeOH/H$_2$O (1:1). Subsequently the pale yellow reaction mixture was stored at 8°C for few days to obtain the colorless crystals of **ZnT** as an insoluble solid. Yield: 62% (based on Zn(NO$_3$).6H$_2$O). M.p.: 208–210°C (decomp.). Anal. Calcd (%) for C$_{15}$H$_{41}$N$_{24}$O$_{25}$Zn$_3$ (1153.78): C, 15.61; H, 3.58; N, 29.14; found: C, 15.4; H, 3.5; N, 29.2. FT-IR (neat, $\bar{v}$, cm^{-1}): 3628(w), 3274(w), 3124(m), 1641(m), 1541(s), 1389(s), 1305(vs), 1273(s), 1161(m), 1053(m), 1013(m), 630(s) cm^{-1}. Solid-state UV-vis: λ_{max} 220 and 292 nm.
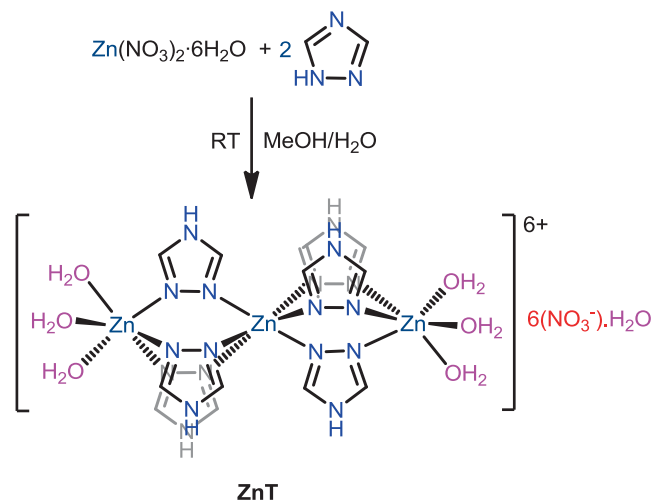
Scheme 1. Synthesis of **ZnT**.

3. Result and Discussion

3.1 *Synthesis and spectral studies*

The synthesis of trinuclear zinc compound **ZnT** was accomplished by layering 1,2,4-triazole solution in MeOH to a solution of $Zn(NO_3)_2.6H_2O$ in H_2O at RT (scheme 1). Insoluble colorless crystals were obtained at 8°C in good yield (60%). The purity of bulk sample was confirmed by CHN analysis. Furthermore, the solid state structure was confirmed by FT-IR, solid-state UV-vis, TGA and single crystal X-ray diffraction techniques. FT-IR spectrum shows a characteristic peak for the N—H stretching frequency at 3124 cm^{-1}. The presence of free NO_3^- ions (1389 cm^{-1}) and water molecules (3625 and 3274 cm^{-1}) are confirmed by FT-IR. Solid-state UV-visible absorption spectra of **ZnT** is depicted in figure 1a that shows two absorption bands centered at 220 and 292 nm, which can be assign to the spin-allowed intra-ligand π to π^* transition.

3.2 *Thermogravimetric analyses*

In order to understand the thermal stability of **ZnT**, thermo gravimetric analysis (TGA) was carried out from 30—1000°C at 10°C/min under N_2 atmosphere (figure 1b). The decomposition pathway of **ZnT** occurs through well defined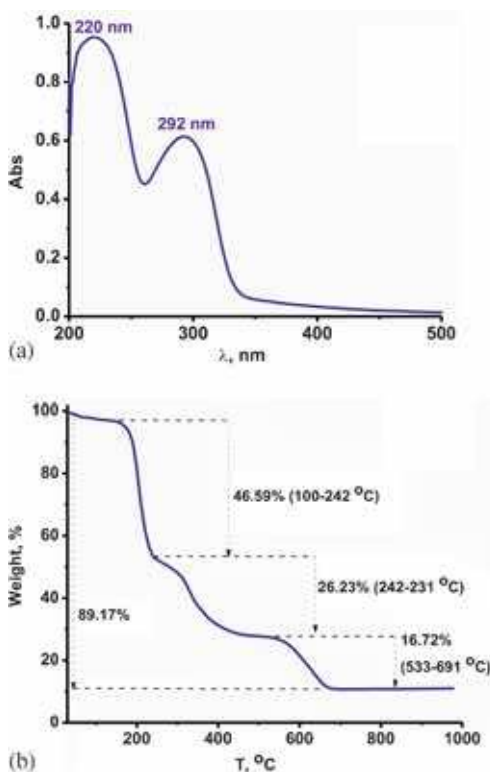 three steps, from 100 to 242°C with 47% weight loss, from 242 to 231°C with 26% weight loss and from 533 to 691°C with 17% weight loss. The total weight loss is 90%. A small weight loss near about ~2% till 100°C can be attributed to loss of moisture. The weight loss of about 47% from 100–242°C can be ascribed to the loss of six NO_3^- and seven H_2O molecules, which is close to the calculated weight percentage (43%) for six NO_3^- and seven H_2O. Subsequently, weight loss of 33% in two stages from 242 to 691°C can be assigned to the decomposition of triazole ligands.

3.3 *Description of the crystal structure*

The solid-state structure of **ZnT** was unambiguously determined by the single crystal X-ray diffraction technique (figures 2 and 3). Compound **ZnT** crystallizes in the monoclinic space group *P21/n* and the asymmetric unit consists of nearly $[Zn_{1.5}(Htrz)_3(H_2O)_3]\cdot(NO_3)_3\cdot H_2O$ (table 1).[12,13] The selected bond lengths and angles are assembled in table 2. The molecule is a hexa cationic

Figure 1. (a) Solid state UV-vis absorption spectrum of **ZnT**. (b) TGA profile of **ZnT**.
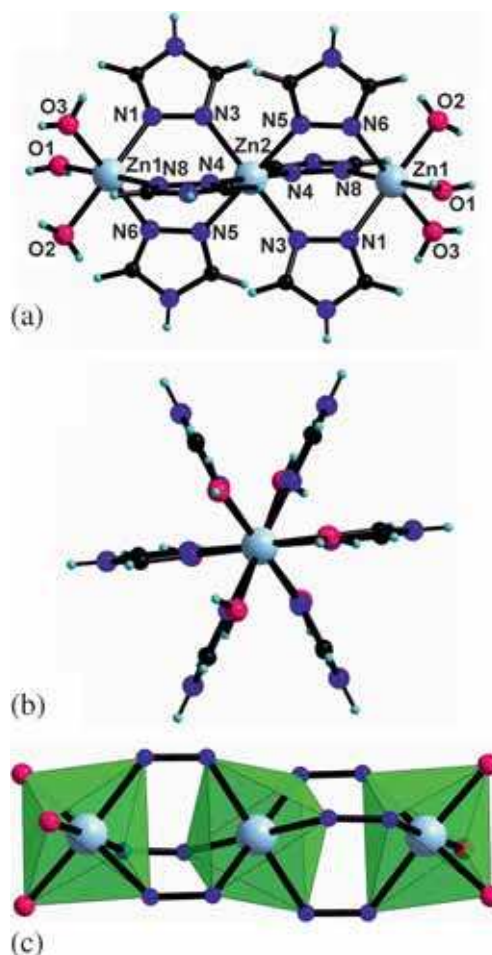
Figure 2. (a) Molecular structure of **ZnT**. The three NO_3^- and one water molecule are omitted for clarity; (b) Molecular structure of **ZnT** viewed along Zn axis. The three NO_3^- and one water molecule are omitted for clarity; (c) The core structure of **ZnT**.
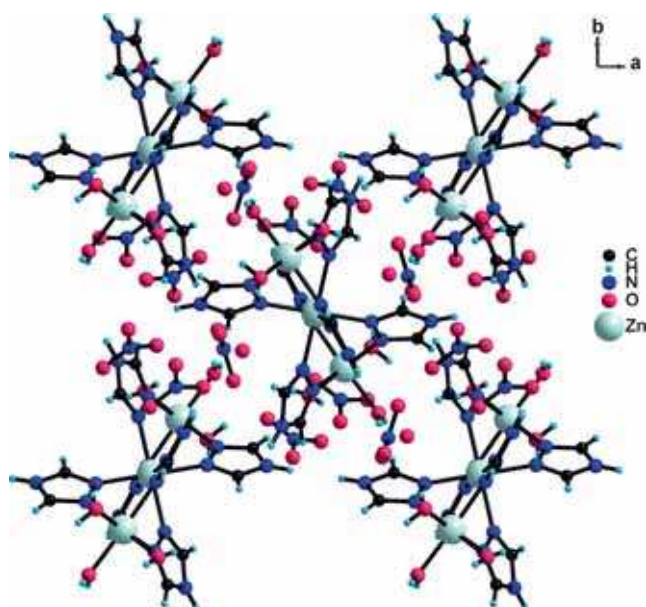
Figure 3. The molecular packing of **ZnT** view along c axis.

zinc trimetallic assembly connected by 1,2,4-triazole ligands with three-fold centro-symmetry along the zinc center (figure 2b). 1,2,4-triazole acts as a μ^2 bridging ligand to connect zinc centers in a straight line. Zinc atoms are hexacoordinated with two types of coordination environments, namely, homoleptic (Zn(2)) and heteroleptic (Zn(1)) coordination environments (figure 2c). Coordination environment of central zinc atom, Zn(2) is fulfilled by six μ^2 bridging 1,2,4-triazole ligands, while the Zn(1) is satisfied by three water molecules and three μ^2 bridging 1,2,4-triazole ligands. Central zinc atom (Zn(2)) shows nearly perfect octahedron geometry, while the terminal zinc atoms (Zn(1)) are slightly distorted. As shown in figure 2c, the orientation of Zn(2) octahedron is different from that of Zn(1). The Zn to Zn separation is 3.8101(8) Å, which is about 1.5 Å shorter than the typical Zinc-Zinc bond distance found in dizincocenes R$-$Zn$-$Zn$-$R.[14] The Zn–N distances fall in the range from 2.189(3) Å (N(3)–Zn(2)) to 2.118(3) Å (N(8)–Zn(1)) and the average Zn–N distance is 2.151 Å. The Zn–O distances are in the range from 2.071(3) to 2.123(3) Å. The N–Zn(2)–N bond angles around Zn(2) varies from 89.43(11)° to 91.25(11)°. The O–Zn(1)–O bond angles around Zn(1) falls from 87.22(14)° to 90.93(15)°. The O–Zn(1)–N bond angle around Zn(1) shows a wide range from 86.40(13)° to 91.16(13)°. The N–Zn(1)–N bond angle around Zn(1) also exhibits a wide range from 89.32(12)° to 94.20(11)°.

3.4 *Structural comparisons*

The molecular structure of **ZnT** is comparable with the counter ion of the recently reported decavanadate complex,

Table 3. Comparison of important bond lengths and angles of **ZnT**, **ZnT^E** and **ZnT^V**.

	ZnT	**ZnT^{E10}**	**ZnT^{V11}**
Bond lengths (Å)			
d Zn to Zn	3.810	3.805	3.815
av. d Zn–N	2.151	2.146	2.149
av. d Zn–OH$_2$	2.096	2.120	2.118
Bond angles (deg)			
∠N–Zn–N range	89.32(12) to 94.20(11)	89.3(1) to 92.0(1)	87.1(2) to 95.92(19)
∠H$_2$O–Zn–OH$_2$ range	87.22(14) to 90.93(15)	84.7(1)	82.20(19) to 93.01(17)
Torsion angles (deg)			
Zn–N–N–Zn	8.86, 1.55, 2.50, –8.86, –1.55, –2.50	7.4	9.52, 2.51, 3.19, –0.62, –6.11, –5.99

ZnT^V, where the $[Zn_3(Htrz)_6(H_2O)_6]^{6+}$ was formed unexpectedly.[11] The important structural matrices of **ZnT**, **ZnT^V** and **ZnT^E** are listed in table 3. Although, in a way the zinc trimer core $[Zn_3(Htrz)_6(H_2O)_6]^{6+}$ in **ZnT** looks similar to that of **ZnT^V**, surprisingly, the structural metrics of **ZnT** is considerably different from **ZnT^V**. For example, the Zn–N bond distances in **ZnT^V** are not equal and twelve different bond distances were observed, while six different bond distances of Zn–N are observed in **ZnT**. Unlike **ZnT**, the six different Zn–OH$_2$ bond distances are noticed in **ZnT^V**. However, the average zinc to zinc separation, Zn–N and Zn–OH$_2$ bond distances of **ZnT**, **ZnT^V** and **ZnT^E** are nearly comparable. Notably, considerable deviations in the N–Zn–N and H$_2$O–Zn–OH$_2$ bond angles are observed between **ZnT**, **ZnT^V** and **ZnT^E**. Similarly, the Zn–N–N–Zn torsion angles of **ZnT**, **ZnT^V** and **ZnT^E** are not comparable.

4. Conclusion

In summary, the first rational synthesis of well defined hexanitrate salts of $[Zn_3(Htrz)_6(H_2O)_6]^{6+}$ (**ZnT**) is reported. Solid state structure of **ZnT** revealed that the formation of a rare zinc trimer bridged by six 1,2,4-triazole ligands, where the zinc atoms are on the same line. Furthermore, for the first time the spectral and thermal properties of **ZnT** are reported.

Supporting Information

FT-IR spectrum and CheckCIF report are available free of charge via the Internet at www.ias.ac.in/chemsci. CCDC 944805 contains the supplementary crystallographic data for this paper. This data can be obtained free

of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

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