

Communication

Hexnuclear Cadmium(II) Cluster Constructed from Tris(2-methylpyridyl)amine (TPA) and Azides

Franz A. Mautner ^{1,*}, Roland C. Fischer ², Bailey R. Williams ³, Salah S. Massoud ^{3,4,*} and Nahed M. H. Salem ⁴

- ¹ Institut für Physikalische and Theoretische Chemie, Technische Universität Graz, A-8010 Graz, Austria
- ² Institut für Anorganische Chemie, Technische Universität Graz, Stremayrgasse 9/V, A-8010 Graz, Austria; roland.fischer@tugraz.at
- ³ Department of Chemistry, University of Louisiana at Lafayette, P.O. Box 43700 Lafayette, LA 70504, USA; bailey.williams3@louisiana.edu
- ⁴ Department of Chemistry, Faculty of Science, Alexandria University, P.O. Box 21511 Moharam Bey, Alexandria, Egypt; nahed_s@yahoo.com
- Correspondence: mautner@tugraz.at (F.A.M.); ssmassoud@louisiana.edu (S.S.M.); Tel.: +43-316-4873-8234 (F.A.M.); +1-337-482-5672 (S.S.M.); Fax: +43-316-4873-8225 (F.A.M.); +1-337-482-5676 (S.S.M.)

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Abstract: A novel rare hexa nuclear cadmium(II)–azide cluster, $[Cd_6(TPA)_4(\mu_3-1,1,3-N_3)_4(\mu_2-1,1-N_3)_6](ClO_4)_2 \cdot 2H_2O$ (**1**) was isolated and structurally characterized, in which the azide ligands reveal μ -1,1,3- and μ -1,1-N₃ bridging modes.

Keywords: cadmium; bridged azide; poylnuclear; cluster; X-ray; luminescence emission

1. Introduction

The construction of discrete of polynuclear metal cluster complexes, in many cases leads to unpredictable intriguing architecture topologies [1–10]. The extent of nuclearity of this class of compounds depends on many factors such as metal ion (oxidation state, coordination number and geometry), nature of coligands and bridging linkers, as well as the reaction conditions such as temperature, solvent and stoichiometry [1–10]. The ligand's nature includes types of donor atoms, denticity, flexibility, shape and size. Thus, the experimental approach for designing a cluster with a specific number of metal atoms within the core of the cluster and its dimensionality is a challenging process, which may depend on the combination of appropriate choice of some of the mentioned factors [2]. However, aside from the subtle complications associated with the design of these clusters, they show promising potential applications in the fields of magnetism, catalysis, gas adsorption and luminescence [11–22].

Over the past three decades, attention was focused on group 12 of d¹⁰ metal ions like zinc and cadmium for the design of polymers, clusters and metal-organic frameworks (MOFs) [1–7,19–24]. A series of polymeric cadmium-azides of different dimensionality MOFs with tri- [25–31], tetra- [25,32], penta- [33] and hexa-nuclear clusters [3,34] have been constructed by the reactions of Cd(II) salts, organic coligands and azide ion linkers. Moreover, 1D coordination polymers of Cd₆ chair-shape cluster [Cd₆(2-Acpy)₄(N₃)₁₂]_n(H₂O)_{2n}·(CH₃OH)_n and their corresponding pentadecanuclear Cd₁₅ crown-like cluster [Cd₁₅(2-Acpy)₁₂(N₃)₃₀]_n·(CH₃OH)_n were isolated with 2-acetylpyridine (2-Acpy) under slightly different stoichiometric conditions [2,3]. An interesting series of discrete cadmium-azide clusters with diverse nuclearity and poly-azide-connectors containing tri- [35,36], tetra- [37,38], penta- [35], hexa- [39], hepta- [40] and even octa-cadmium centers [41] were also reported. Herein,



we report the synthesis, crystal structure and the luminescent emission of the novel hexanuclear cluster, $[Cd_6(TPA)_4(\mu_3-1,1,3-N_3)_4(\mu_2-1,1-N_3)_6](ClO_4)_2 \cdot 2H_2O(1)$, where TPA = tris(2-methypyridyl)amine.

The complex was isolated as colorless single crystals by reacting a methanolic solution containing $Cd(ClO_4)_2 \cdot 6H_2O$ and TPA and an aqueous NaN₃ solution in a 1:1:2 molar ratio. The IR spectrum of the complex reveals very strong band around 2020 cm⁻¹ due to the asymmetric stretching vibration of the azido group, $v_{as}(N_3)$. The split of this band into 2045 and 2020 cm⁻¹ results from the presence of two bonding azido modes $\mu_{1,1,3}$ -N₃ and $\mu_{1,1}$ -N₃ modes (see X-ray section). The complex showed two very weak broad bands around 3610 and 3330 cm⁻¹, which are attributed to v(O-H) stretching of hydrates. In addition, the complex exhibits two strong vibrational bands at 1087 and 1051 cm⁻¹ resulting from the v(Cl-O) of the ClO_4^- counter ions. The split of the bands is most likely attributed to the decreased symmetry of the ClO_4^- due to its involvement in H-bonding with the water of crystallization. The purity of the complex **1** was supported by the good agreement between its experimental and simulated X-ray powder diffraction patterns (Figure S1, Supplementary Materials). The isolated cluster was found to be very stable in air as well as in aqueous or methanolic solutions, where no changes in its UV spectrum were observed over a period of at least four days.

The single crystal X-ray structure analysis (Table S1, Supplementary Materials) reveals the existence of a centrosymmetric cationic $[Cd_6(TPA)_4(\mu_3-1,1,3-N_3)_4(\mu_2-1,1-N_3)_6]^{2+}$ cluster unit (Figure 1), where the three crystallographic independent Cd(II) deviate by 0.066, 0.203 and 0.017 Å for Cd1, Cd2 to Cd3, respectively, from the mean plane of the metal centers. The central Cd2 and Cd2' pair is linked by the N11 and N11' atoms of two $\mu_{1,1,3}$ -N₃ bridging azide groups. Each six-coordinated Cd2 is further connected with Cd3 by a single $\mu_{1,1}$ -N₃ bridge and with Cd1 by a $\mu_{1,1}$ -N₃ double bridge. Coordination number (C.N.) six is completed by a $\mu_{1,1,3}$ -N₃ azide group, which further connects Cd2 with Cd1 by its $\mu_{1,3}\text{-}N_3$ and with Cd3' by its $\mu_{1,1}\text{-}\text{bonding}.$ Thus, the external Cd1 is ligated by two $\mu_{1,1}$ and one $\mu_{1,1,3}$ -azide bridges, whereas Cd3 is ligated by two $\mu_{1,1,3}$ and one $\mu_{1,1}$ -azide bridges. The C.N. seven around Cd1 and Cd3 centers is achieved by the four N-donor atoms of the Tris(2-methylpyridyl)amine (TPA) molecule, respectively (Figure 2). The intra-cluster metal-metal separations are: Cd1-Cd2 3.7648(10), Cd2···Cd3 4.3099(11), Cd2···Cd3' 4.4160(11), Cd2···Cd2' 3.5271(10), Cd1···Cd3 7.2601(18), Cd1…Cd3' 9.277(2), Cd1…Cd1' 10.918(2) and Cd3…Cd3' 7.982(2) Å. The Cd2-N bond distances in its distorted octahedron vary from 2.287(3) to 2.418(3) Å, with shorter bond distances formed to N5, N8 and N14 atoms of $\mu_{1,3}$ -N₃ groups. The Cd-N bond distances of the seven-coordinated Cd1 and Cd3 vary from 2.325(3) to 2.607(3) Å (Table S2). Both coordination figures may be described as distorted capped trigonal prisms, with shortest Cd-N bonds formed to pyridine-N atoms of TPA ligands, while the longest bond distances are Cd1-N5 [2.607(3) Å] and Cd3-N13 [2.547(3) Å]. The N-Cd-N of Cd1 and Cd3 vary from 68.99(11) to 164.04(11)°. The Cd-N-Cd and Cd-N-N bond angles are in the range from 95.86(12) to $132.52(14)^{\circ}$ and from 106.0(2) to $135.6(3)^{\circ}$, respectively. The torsion angles are: Cd2-N11···N13-Cd3 = 54.0°, Cd2'-N11···N13-Cd3 = -49.6°, Cd2'-N17···N19-Cd1' = 0.7° and Cd3-N17···N19-Cd1' = -176.4° . The azide groups are asymmetric with N α -N β bonds from 1.194(4) to 1.218(5) Å and N β -N γ bonds from 1.146(5) to 1.163(5) Å (with N α ligated to two Cd centers). The difference between N-N bonds within the azide groups are 0.032, 0.059 and 0.067 Å, for the three $\mu_{1,3}$ -N₃ and 0.032 and 0.047 Å for the two $\mu_{1,1,3}$ -N₃ azide groups. The N-N-N bond angles vary from 178.1(4) to 179.6(5)° (Table S2).



Figure 1. Molecular plot of $[Cd_6(TPA)_4(\mu_3-1,1,3-N_3)_4(\mu_2-1,1-N_3)_6]^{2+}$ cluster unit. Symmetry code ('): 1 - x, 1 - y, 1 - z.



Figure 2. The Cd-N core of $[Cd_6(TPA)_4(\mu_3-1,1,3-N_3)_4(\mu_2-1,1-N_3)_6]^{2+}$ cluster unit. Symmetry code ('): 1 - x, 1 - y, 1 - z.

The $[Cd_6(TPA)_4(\mu_{1,1,3}N_3)_4(\mu_{1,1}N_3)_6]^{2+}$ units co-crystallize with ClO_4^- counter anions and disordered water molecules in a 1:2:2 molar ratio. The packing of the building blocks is stabilized by various types of hydrogen bonds and $\pi \cdots \pi$ ring-ring interactions between pyridyl moieties of the TPA molecules (Figure 3, Tables S3 and S4).



Figure 3. Packing plot of [Cd₆(TPA)₄(µ₃-1,1,3-N₃)₄(µ₂-1,1-N₃)₆](ClO₄)₂·2H₂O (1).

The photoluminescence emission spectra of solid samples of the title compound, free TPA and NaN₃ are represented in Figure 4 (Perkin-Elmer Lamde LS55 spectrofluorometer, excitation at $\lambda_{ex} = 366$ nm). Sodium azide shows very weak emission with a flat plateau from approx. 430–580 nm. The TPA ligand exhibits medium intense emission maximum at 548 nm and a shoulder at ~445 nm. The title complex 1 shows enhanced emission intensity with a maximum at 505 nm and a second maximum at 438 nm. The observed enhancement of luminescent intensity bands of complex 1 compared to the free TPA ligand is most likely attributed to the increased Cd-N_{py} bond strength, which effectively increases the rigidity of the ligand and hence reduces the non-radiative decay of the intra-ligand excited state.



Figure 4. The emission spectra of solid samples of the Cd6 complex **1**, free Tris(2-methylpyridyl)amine (TPA) and NaN₃ (λ_{ex} = 366 nm).

2. Synthesis of [Cd₆(TPA)₄(µ₃-1,1,3-N₃)₄(µ₂-1,1-N₃)₆](ClO₄)₂·2H₂O (1)

An aqueous solution of NaN₃ (0.065 g, 1 mmol in 10 mL H₂O) was added to a mixture containing equimolar amounts of Cd(ClO₄)₂·6H₂O (0.210 g, 0.5 mmol) and TPA (0.145 g, 0.5 mmol) dissolved in MeOH. The resulting solution was heated for 10 min on a steam-bath, filtered through celite then,

allowed to crystalize at room temperature. Colorless single crystals were obtained within 2–4 days. These were collected by filtration, washed with propan-2-ol, Et₂O and dried in air (an overall yield is about 70%). Anal. Calcd for $C_{72}H_{76}Cd_6Cl_2N_{46}O_{10}$ (2491.02 g/mol): C, 34.72; H, 3.08; N, 25.86. Found: C, 34.82; H, 3.23; N, 25.49%. IR bands (ATR, cm⁻¹): 3610 (w,b), 3330 (w,b) v(O-H) stretching; 3050 (vw), 2914 (vw), 2851 (vw) v(C-H); 2045 (vs), 2020 (vs) v(N3); 1602 (s), 1575 (m) 1482 (m), 1443 (s), 1333 (w), 1288 (w), 1158 (w), 1087 (vs), 1051 (s) v(Cl–O) (ClO₄⁻⁻); 1015 (m), 956 (w), 900 (w), 839 (w), 768 (vs).

Caution! Salts of perchlorate and azides as well as their metal complexes are potentially explosive and should be handled with great care and in small quantities.

To summarize, we have successfully synthesized and structurally characterized the novel hexa-nuclear Cd6 cluster complex **1**. To the best of our knowledge, there was only one hexa nuclear Cd6 cluster $Mn_{13}Cd_6$; $[Cd^{II}_6Mn^{II}_9Mn^{III}_4(L)_{18}(OH)_{12}(N_3)_6](ClO_4)_6\cdot 12CH_3CN$ (HL = 1-(hydroxymethyl)-3,5-dimethylpyrazole), where the outer shell ring contains a random mixture averaging six Cd and six Mn [39]. The isolated title complex **1** has unique structure features with all metal centers consist of only Cd(II) ions in six- and seven-coordination numbers as well as the existence of azides in two $\mu_{1,1}$ -and $\mu_{1,1,3}$ -bridging modes. At this point, we should mention that this work is still in progress in order to explore the influence of the counter ions, substituents in the TPA coligand and the nature of the pseudo-halide bridges.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4352/10/4/317/s1, X-ray crystal structure analysis of compound **1**, Table S1: Crystallographic data and processing parameter, Table S2: Selected bond lengths (Å) and angles (°), Table S3: $\pi \cdot \cdot \pi$ ring $\cdot \cdot \cdot r$ ing interactions, Table S4: Possible hydrogen bonds, Figure S1: Observed (bottom) and simulated (top) X-ray powder diffraction pattern. CCDC 1990313 contains the supplementary crystallographic data for **1**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Author Contributions: F.A.M. and R.C.F. performed the X-ray structural analysis. B.R.W., S.S.M. and N.M.H.S. contributed in the synthesis and characterization of the compound. F.A.M., S.S.M. and N.M.H.S. contributed to the writing of the manuscript. All authors have read and agreed to the published version of the manuscript.

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