Dalton Transactions





Cite this: DOI: 10.1039/c7dt01138e

A sandwich-shaped M_3L_2 zinc(II) complex containing 1,3,5-tris(dimethyl(pyridin-3-yl)silyl)benzene: selective photoluminescence recognition of diiodomethane[†]

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Received 30th March 2017, Accepted 5th April 2017 DOI: 10.1039/c7dt01138e

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Self-assembly of Zn(ClO₄)₂ with 1,3,5-tris(dimethyl(pyridin-3-yl)silyl)benzene (**L**) as a new C₃-symmetric tridentate N-donor gives rise to a discrete sandwich-shaped M_3L_2 architecture, [Zn₃(μ -OH)₃L₂](ClO₄)₃·4CH₃CN· 2H₂O. Its blue photoluminescence is significantly quenched only by CH₂I₂ among the various small molecules, CH₂Cl₂, CH₂Br₂, CHCl₃, 1,2-dichloroethane, EtOH, CH₃CN, benzene, toluene, and phenol.

Introduction

Diiodomethane (CH_2I_2) is known to be unsafe to human health as well as destructive to the atmosphere's oxidative capacity.¹ Nevertheless, it is a suitable chemical for use in density measurements of minerals and as a carbene transfer reactant in Simmons-Smith-type cyclopropanations.²⁻⁶ In recent years, the photo-excitation of CH2I2 and its related photo-decomposed chemical species electrons, CH₂I₂ cations, and iodomethyl radicals has been a hot research topic.⁷⁻¹¹ Thus, research chemists consider a comprehensive recognition of CH₂I₂ an urgent priority. Meanwhile, several recent reports, notably, have demonstrated that transition metal complexes' photo-luminescence is useful to develop sensors for specific chemicals.¹²⁻¹⁵ To the best of our knowledge, the field still lacks systematic information on CH₂I₂ molecule recognition *via* a novel type of luminescent $zinc(\pi)$ complex architecture. Thus far, significant coordination architectures with task-specific reaction-vessel, catalyst, ionophore,⁵ molecular capsulation, and molecular recognition functions, tantalizingly, have been synthesized by self-assembly of zinc(II) ions with polydentate donors taking into consideration various factors such as counteranions, mole ratios, reaction temperature, and reaction solvents.¹⁶⁻²² In this context, we have carried out preliminary research on CH2I2 recognition of the intriguing sandwich-shaped M_3L_2 zinc(II) architecture of a new C_3 -symmetric tridentate ligand. We describe a new class of this architecture that can be utilized

Department of Chemistry, Pusan National University, Busan 46241, Korea. E-mail: oksjung@pusan.ac.kr for the selective photoluminescence recognition of CH₂I₂. Generally, zinc(II) complexes have been investigated and deemed to be appropriate candidates for tetrahedral-binding Lewis acids, metalloenzymes, zinc-finger proteins, transmetallation, photoluminescence materials, and homogeneous catalysts in the transesterification of a wide range of esters with alcohols.^{23–31}

Experimental

Materials and measurements

All chemicals including zinc(II) perchlorate hexahydrate $(Zn(ClO_4)_2)$, *n*-butyllithium, and 3-bromopyridine were purchased from Sigma-Aldrich and used without further purification. 1,3,5-Tris(chlorodimethylsilyl)benzene (2) was prepared via a literature method.³² Elemental analyses (C, H, and N) were performed on crystalline samples at the KBSI Pusan Center using a Vario-EL III analyzer. ¹H (300 MHz) and ¹³C (75 MHz) NMR spectra were obtained on a Varian Mercury Plus 300. Infrared (IR) spectra were recorded on a Nicolet 380 FT-IR spectrophotometer using samples prepared as KBr pellets. Thermal analyses were undertaken under a nitrogen atmosphere at a scan rate of 10 °C min⁻¹ using a Labsys TGA-DSC 1600. Excitation and emission spectra were acquired on a FluoroMate FS-2 spectrofluorometer. Electrospray time of flight ionization mass spectrometry (ESI-TOF-MS) was performed on a Synapt G2 mass spectrometer (Waters) at the Ochang Center, KBSI. Timeresolved fluorescence spectra were recorded on an FL920-TCSPC spectrofluorometer (Edinburgh Instruments) using a 375 nm laser source for excitation, as listed in Table S3.[†]

Synthesis of 1,3,5-tris(dimethyl(pyridin-3-yl)silyl)benzene (L)

To a solution of 3-bromopyridine (2.89 mL, 30 mmol) in dry diethyl ether (75 mL) under a nitrogen gas atmosphere,

Published on 20 April 2017. Downloaded by Middle East Technical University (Orta Dogu Teknik U) on 20/04/2017 21:12:46.



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[†] Electronic supplementary information (ESI) available: X-ray crystallographic data, ORTEP drawings, thermal analysis and differential scanning calorimeter data, FT-IR spectra, photoluminescence spectra, and fluorescence lifetime of $[Zn_3(\mu-OH)_3L_2]$ -(ClO₄)₃·4CH₃CN·2H₂O. CCDC 1534794. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c7dt01138e

n-butyllithium (12 mL of a 2.5 M solution in n-hexane, 30 mmol) was added dropwise at -78 °C. The resulting mixture was allowed to warm to 0 °C, at which temperature it was stirred for 1 h 30 min. Then, 1,3,5-tris(chlorodimethylsilyl) benzene (15 mL, 10 mmol) was slowly added to the above yellow suspension at -78 °C, and the reaction mixture was stirred at room temperature for 12 h. Distilled water (40 mL) was subsequently added, and the organic layer was separated. The organic solution was washed with water several times and then dried over anhydrous magnesium sulfate. Evaporation of the solvent produced a reddish-brown oil, which was then purified by column chromatography using ethyl acetate as an eluent. The resulting solution was evaporated, thus affording crystalline solid 1,3,5-tris(dimethyl(pyridin-3-yl)silyl)benzene (L) in 35% yield. Anal. calcd for C₂₇H₃₃N₃Si₃: C, 67.03; H, 6.87; N, 8.68%. Found: C, 67.20; H, 6.77; N, 8.70%. ESI-TOF-MS m/z 484.2059 (calc. 484.202 for $[L + H^+]^+$). IR (KBr pellet, cm⁻¹): 2956m, 1574m, 1558w, 1397m, 1372w, 1250m, 1144w, 1123m, 1026w, 844s, 828s, 797m, 779s, 762m, 713m, 657m, 623w, 422s. ¹H NMR (Me₂CO-d₆, 300 MHz,δ): 8.64 (s, 3H), 8.55 (d, ${}^{3}J = 5.1$ Hz, 3H), 7.84 (s, 3H), 7.81 (d, ${}^{3}J = 5.1$ Hz, 3H), 7.30 (dd, ${}^{3}J$ = 5.1 Hz, 4.2 Hz, 3H), 0.58 (s, 18H). ${}^{13}C$ NMR (CDCl₃, 72 MHz, ppm,δ): 154.50, 150.30, 141.90, 140.88, 135.85, 133.00, 123.35, -2.54.



Preparation of [Zn₃(µ-OH)₃L₂](ClO₄)₃·4CH₃CN·2H₂O

An acetonitrile solution (10 mL) of $\text{Zn}(\text{ClO}_4)_2$ (1.396 g, 3.75 mmol) was slowly diffused into a methanol solution (10 mL) of L (1.210 g, 2.5 mmol). After 2 days, colorless crystals suitable for X-ray crystallography were obtained (2.213 mg, 52% yield). Mp 333 °C (dec.). Anal. calcd for $\text{C}_{62}\text{H}_{83}\text{Cl}_3\text{N}_{10}\text{O}_{16}\text{Si}_6\text{Zn}_3$: C, 43.92; H, 4.93; N, 8.26%. Found: C, 44.20; H, 4.70; N, 8.13%. ESI-TOF-MS *m*/*z* 646.0753 (calc. 646.063 for $[[\text{Zn}_3(\mu\text{-OH})_3\text{L}_2]$ (ClO₄)₃ – 2(ClO₄⁻) – OH⁻ – H⁺]²⁺), 1395.0936 (calc. 1398.081 for $[[\text{Zn}_3(\mu\text{-OH})_3\text{L}_2](\text{ClO}_4)_3 - \text{ClO}_4^- - \text{OH}^- - \text{H}^+]^+)$. IR (KBr pellet, cm⁻¹): 3541br, 2956w, 1593m, 1404m, 1255m, 1103s, 839s, 773m, 705m, 625m, 424m. ¹H NMR (Me₂CO-d₆, 300 MHz, δ): 8.45 (d, ³*J* = 7.6 Hz, 3H) 8.21 (s, 3H) 8.17 (d, ³*J* = 4.1 Hz, 3H) 7.97 (s, 3H) 7.60 (dd, ³*J* = 6.0, 6.0 Hz, 6H) 0.74 (s, 18H).

X-ray crystallography

X-ray data were collected using a Bruker SMART automatic diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å) and a CCD detector at -25 °C. Thirty-six frames of two-dimensional diffraction images were collected and processed to obtain the cell parameters and orientation matrix. The data were corrected for Lorentz and polarization effects. The absorption effects were corrected using the multi-scan method (SADABS).³³ The structures were solved using direct

methods and refined by full-matrix least squares techniques (SHELXL 2014/07).³⁴ The non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were placed in calculated positions and refined only for the isotropic thermal factors. The crystal parameters and procedural information corresponding to the data collection and structure refinement are listed in Table S1,† and the relevant bond lengths and angles are listed in Table S2.†

Results and discussion

Synthesis

The novel C_3 -symmetric tridentate 1,3,5-tris(dimethyl(pyridin-3-yl)silyl)benzene (L) was obtained by three-step synthesis in overall 35% yield. Self-assembly of $Zn(ClO_4)_2$ with the L as a C_3 -axis tridentate N-donor in an acetonitrile and methanol solution at room temperature produced the discrete sandwichshaped M_3L_2 architecture of $[Zn_3(\mu-OH)_3L_2](ClO_4)_3\cdot 4CH_3CN\cdot$ $2H_2O$ shown in Scheme 1. The reaction was initially performed in a 1 : 1 mole ratio of $Zn(\pi)$: L and the lack of any significant effects on the products from either the mole ratio or concentrations indicated that the architecture is a thermodynamically stable chemical species.

Crystal structures

The crystal structure of $[Zn_3(\mu-OH)_3L_2][ClO_4)_3\cdot 4CH_3CN\cdot 2H_2O$ consists of three zinc(II) ions, two ligands, three hydroxo anions, three perchlorate anions, and solvate molecules (Fig. 1). The local geometries of the zinc(II) cation is a typical tetrahedral arrangement with two oxygen atoms from the hydroxo anions and two nitrogen atoms from the ligands (Zn–N = 2.023(3)–2.032(3) Å, Zn–O = 1.899(3)–1.930(3) Å, bond angles around Zn(II) = 102.9(1)–123.3(1)°). The structure has a tripod tridentate ligand, and a 6-membered cyclic Zn₃(μ -OH)₃ motif (Zn···Zn = 3.3803(6)–3.4284(6) Å; see ESI Fig. S1†), and thus forms a sandwich-type M₃L₂ architecture. The Zn₃(μ -OH)₃ ring adopts a puckered-conformation, which is similar to that of the known Zn₃(μ -OH)₃ species.³⁵ The perchlorate anions act



Scheme 1 Synthetic scheme of $[Zn_3(\mu-OH)_3L_2](ClO_4)_3$ -4CH₃CN-2H₂O and photoluminescence properties for molecular recognition.



Fig. 1 Crystal structures of $[Zn_3(\mu-OH)_3L_2](ClO_4)_3\cdot 4CH_3CN\cdot 2H_2O$. Relevant bond lengths: Zn-O = 1.899(3)-1.930(3) Å, Zn-N = 2.023(3)-2.032(3) Å, $O-Zn-O = 102.9(1)-106.1(1)^\circ$, $O-Zn-N = 103.1(1)-123.3(1)^\circ$, $N-Zn-N = 103.6(1)-109.4(1)^\circ$.

as counteranions rather than ligands. The two central phenyl rings are nearly parallel to each other with a dihedral angle of $3.5(2)^\circ$, which arrangement is similar to that of our previous cyclophanes.^{36,37} The pyridyl donors are directed toward the out-of-plane of the C_3 -symmetric facial ligand, and the tilting angle between the central benzene is 76.0(1)–81.8(1)°.

Construction principle

Formation of the 6-membered hydrolyzed $Zn_3(\mu$ -OH)₃ ring can be similarly explained by a report that is available in the literature.³⁵ Hydrolysis is an important factor in the self-assembly reaction and, thus, in the formation of the $Zn_3(\mu-OH)_3$ skeleton. But what is the critical driving force behind the formation of a discrete trimetallic sandwich-type molecule rather than coordination polymers? In the present study, the addition of trace NaOH to the reaction system accelerated the formation of the product. The bridged-hydroxo moiety was probably formed through the hydrolysis of trace water molecules in the reaction system. That is, the basic conditions for the selfassembly accelerated the hydrolysis. A combination of the tetrahedral geometry of zinc(II) ions and the appropriate tridentate ligand seems to be a key role for the formation of a sandwich-shaped Zn(II) complex. Specifically, the meta-position of the N-donor might be the obstacle to the formation of coordination polymers. Also, the size of the perchlorate counteranion seems to partially contribute to the formation of the discrete structure. The colorless crystalline product of [Zn₃(µ-OH)₃L₂](ClO₄)₃·4CH₃CN·2H₂O is air-sensitive and soluble in acetone and methanol. It is dissociated in N,N-dimethylformamide and dimethyl sulfoxide and insoluble in water and chloroform. According to ESI-TOF-MS data in acetone solution, the $[Zn_3(\mu-OH)_3L_2](ClO_4)_3 \cdot 4CH_3CN \cdot 2H_2O$ skeletons along with the respective ligand species were detected (Fig. 2). In the present study, the skeletal decomposition temperature of $[Zn_3(\mu-OH)_3L_2](ClO_4)_3 \cdot 4CH_3CN \cdot 2H_2O$ was about 290 °C, and the solvate acetonitrile and water molecules evaporated within a wide 90-180 °C range (weight loss: calc. 11.8%, found 10.8%) (see ESI Fig. S2[†]). Their infrared (IR) spectra, moreover, were



Fig. 2 ESI-TOF-MS data on the present zinc(1) complex corresponding to $[M-ClO_4^--OH^--H^+]^+$ (red line, calc.; black line, found).

found to be consistent with their structures (see ESI Fig. S3†). The ¹H chemical shifts of $[Zn_3(\mu-OH)_3L_2](ClO_4)_3\cdot 4CH_3CN\cdot 2H_2O$ show up-field shift relative to L and its ¹H NMR spectrum in acetone is consistent with its crystal structure. However, the addition of Me₂SO to the acetone solution initiates dynamic molecular behavior (10:2) and then, finally, dissociation (>10:4), as shown in Fig. 3. L, when irradiated with UV light,



Fig. 3 Partial ¹H NMR spectra of $[Zn_3(\mu-OH)_3L_2](ClO_4)_3\cdot 4CH_3CN\cdot 2H_2O$ upon the addition of Me₂SO-*d*₆ to Me₂CO-*d*₆ at room temperature. The volume ratios of Me₂CO-*d*₆ : Me₂SO-*d*₆ are 0 : 10 (a), 10 : 4 (b), 10 : 3 (c), 10 : 2 (d), 10 : 1 (e), 10 : 0.5 (f), 10 : 0 (g).

displays a weak emission band at $\lambda_{em} = 373 \text{ nm} (\lambda_{ex} = 317 \text{ nm})$ in the solid state. [Zn₃(μ -OH)₃L₂](ClO₄)₃·4CH₃CN·2H₂O shows an intense emission band at $\lambda_{em} = 410 \text{ nm} (\lambda_{ex} = 333 \text{ nm})$ in methanol and an emission band at $\lambda_{em} = 324 \text{ nm} (\lambda_{ex} = 275 \text{ nm})$ in the solid state (Fig. 4; ESI Fig. S4†). The sandwich-shaped complex's emission shows an unusual quenching selectivity to the CH₂I₂ molecule in both methanol and the solid state. Thus, the emission band is blue-shifted relative to the corresponding L.

Recognition behavior via quenching

Recently, significant attention has been paid to $d^{10} \operatorname{zinc}(\pi)$ complexes owing to their various applications in chemical sensors, catalysts, and electroluminescent displays.^{38,39} The complex's emission bands can be ascribed to the ligand-tometal charge transfer (LMCT) as well as the ligand's intrinsic characteristics. Such a significant difference between L and the complex in intensity can be attributed to the effective increase of the Zn-N bond rigidity and the reduction in the loss of energy through radiationless decay.²¹ Although the exact nature of the interactions between the CH2I2 molecule and the complex in either methanol or the solid state cannot be established at this moment, the high selectivity of the photoluminescence of the zinc(u) complex towards CH_2I_2 can be attributed to the reasonable matching between the two species. General luminescence quenching of a metal complex can occur in either of two ways:40 (1) instantaneous quenching when a quencher CH_2I_2 lies within a critical radius R_c containing n molecules around the complex; (2) diffusive quenching caused by the interaction of diffusing excited fluorophore and quencher CH₂I₂ molecules. Thus, a fraction of the complex excited at any given moment is quenched instantaneously and the remaining ones either undergo diffusional quenching or spontaneous decay. Among the various small chemicals such



Fig. 4 Fluorescence excitation (black line) and emission (blue line) spectra of $[Zn_3(\mu-OH)_3L_2](ClO_4)_3 \cdot 4CH_3CN \cdot 2H_2O$ in a methanol solution in the presence of various CH_2I_2 concentrations (0; 4.09×10^{-5} ; 8.15×10^{-5} ; 1.22×10^{-4} ; 1.62×10^{-4} ; 2.02×10^{-4} ; 2.41×10^{-4} ; 2.80×10^{-4} ; 3.19×10^{-4} ; 3.58×10^{-4} ; 3.97×10^{-4} ; 4.36×10^{-4} mol L^{-1}); inset: Stern–Volmer plots of I_0/I versus CH_2I_2 concentration, [Q], for the complex in methanol.

as CHCl₃, CH₂Cl₂, 1,2-dichloroethane, EtOH, CH₃CN, benzene, toluene, and phenol (see ESI Fig. S5†), only CH₂I₂ quenches the emission of the complex. In order to establish the quenching mechanism, the fluorescence quenching data were analyzed in this study using the Stern–Volmer equation (eqn (1)),⁴¹

$$\frac{I_0}{I} = 1 + K_{\rm SV}[\mathbf{Q}] \tag{1}$$

where I_0 and I denote the emission intensity before and after quencher (CH_2I_2) addition, respectively, [Q] is the quencher concentration, and K_{SV} is the Stern–Volmer constant defining the quenching efficiency. The Stern–Volmer constant K_{SV} = 1131.4 was evaluated from the initial linear part of the quenching curve, which indicates dynamic quenching.42,43 The fluorescence decays of [Zn₃(µ-OH)₃L₂](ClO₄)₃·4CH₃CN·2H₂O in various CH₂I₂ concentrations in a methanol solution were all fit to biexponential curves (see ESI Fig. S6[†]). The lifetime (τ) shortening after the addition of CH2I2 as a quencher is due to the dynamic quenching mechanism.44 At higher concentrations of the quencher, a non-linear plot of the Stern-Volmer equation suggests the presence of a static quenching component. The crystalline solid after several washings with diethyl ether in order to remove CH2I2 is recyclable for additional molecular recognition (see ESI Fig. S7[†]).

Conclusions

This communication provides a proof-of-experiment example of a novel C3-symmetric tris(silyl-pyridyl) tridentate ligand facilitating the formation of a sandwich-shaped M₃L₂ architecture. The sandwich-shaped M₃L₂ Zn(II) complex has interesting structural features, and its strong blue photo-luminescence efficiently recognizes the CH₂I₂ molecule. Although the photoresponse is still far from suitable for practical applications, the uniquely shaped complex, based on the novel ligand, is promising as a photoluminescent sensor for specific small molecules. According to the results, the fluorescence quenching follows the dynamic quenching mechanism. These results could provide important clues to the design of capsule-like self-assemblies having potential catalyst, sensor, and recognition applications. Additional and more systematic studies, for example on the synthesis and coordination frameworks of related ligands, are in progress.

Acknowledgements

This work was supported by a National Research Foundation of Korea (NRF) grant funded by the Korean Government [MEST] (2016R1A2B3009532 and 2016R1A5A1009405).

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