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Design, synthesis and properties of a trinuclear copper(I) cluster with a triazenide ligand

Wen-jun Lei, Xing-wu Tan, Li-jun Han, Shu-zhong Zhan *, Bai-tao Li *

College of Chemistry & Chemical Engineering, South China University of Technology, Guangzhou, 510640, China

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ABSTRACT

The reaction of methyl anthranilate, sodium nitrite, and 2-aminobenzothiazole produces a new triazenide, namely, 1-[(2-carboxymethyl) benzene]-3-[benzothiazole]triazene (HL). In the presence of Et₃N, the reaction of HL and CuCl in THF/methanol gives a trinuclear copper(1) cluster [Cu₃L₃] THF CH₃OH (**1** THF CH₃OH), which has been characterized by X-ray crystallography, cyclic voltammogram and emission spectrum. CV of **1** reveals two reversible waves at -0.06 and 0.83V, which correspond to two one-electron oxidation of Cu₃ units ([Cu₃]⁴⁺/[Cu₃]³⁺) and ([Cu₃]⁵⁺/[Cu₃]⁴⁺), respectively. **1** appears photoluminescent ($\lambda_{max} = 502$ nm) at room temperature.

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The design and synthesis of new ligands that support transition metal complexes and/or clusters are often inspired by systems in bioinorganic, materials, and catalysis chemistry. By designing the appropriate ligand, we can chelate metal centers in special frame and control the electron withdrawal from the metal ion core, thereby modifying the intramolecular exchange interactions. The use of different bridging and well-designed polydentate ligands has afforded an impressive array of nuclear coordination complexes with new architectures. Among them, the triazenide ligands have attracted our attention, as these compounds can serve as a monodentate (a) [1,2], a bidentate chelating (b) [3–7], and a bridging ligands (c) [8–12] (Scheme 1).

With this mind, our work focuses on the sign, synthesis and their reactivity with transition metals of new bridging ligands (Scheme 1d) which can delocalize electron density through their B-bonding network and strongly donate π electron density to the metal atoms and control the organization of polynuclear metal complexes [13].

We have synthesized a new triazenide ligand, 1-[(2-carboxymethyl)benzene]-3-[benzothiazole]triazene (HL) by modification of a literature procedure [14]. The reaction of HL and CuCl in THF/ methanol gives a trinuclear copper(I) cluster **1**. In this communication, we present the synthesis and characterization of HL and its compound **1**, as well as the electrochemical and photoluminescent properties of **1**.

The reaction of methyl anthranilate, sodium nitrite, and 2-aminobenzothiazole gives a triazenide compound (HL) in 69% yield [15] and Fig. s1.¹H NMR spectrum]. In the presence of Et₃N, the reaction of HL and CuCl in THF/methanol provides a red cluster $Cu_{3}^{l}L_{3}$ **1** in good yield [16], which is solvable in DMF, THF, CH₂Cl₂ and CH₃CN.

As shown in Fig. 1, HL contains a rigid N(1) = N(3) double bond and a potential NNNCN donor set, and making it -1 anionic ligand (L⁻) when deprotonated [17]. The N(1)–N(3) and N(2)–N(3) bond distances are 1.313(3) and 1.264(3)Å, respectively. The bond angles of N(2)–N(3)–N(1) and N(4)–C(4)–N(2) are 112.8(2) and 120.9(3)°, respectively.

X-ray quality crystals of 1 were grown from THF/methanol by slow evaporation of the solvent. An ORTEP view of 1, excluding solvent molecules, is illustrated in Fig. 2 [18]. 1 consists of a tricopper $[Cu_3L_3]$ unit, which is supported by three L^- ligands via the 2+1arrangement with one free N=N group. Two L⁻ ligands are bonded in a tri(bidentate) manner bridging three metal centers, and the third L⁻ ligand is bonded in a bis(bidentate) manner bridging two metal centers. The terminal Cu(1) is three coordinated by two nitrogen atoms from two L⁻ ligands and one M-M bond, the Cu-N distances are 1.90(9) and 1.910(8) Å, which are shorter than those found in copper(II) triazenide 1.973 to 2.088 Å [19]. Another terminal Cu(3) is four coordinated by three nitrogen atoms from three L⁻ ligands and one M-M bond, the Cu-N distances are 1.946(9), 1.962(9), and 1.987 (10) Å. The mean central Cu(2) is linked by three nitrogen atoms from three L⁻ ligands and two M-M bonds, the Cu-N distances are 1.958 (9), 1.978(9), 1.997(10) Å.

Unlike some polynuclear metal chain complexes, such as $[Cu(\mu_3-dpa)_4]Cl_2 (\angle Cu(1)-Cu(2)-Cu(3) = 178.12^\circ) (dpa = bis(2-pyridyl) amine ion) [20], and <math>[Pt_3(\mu-dppm)_3]^{2+}$ (Pt-Pt-Pt angles fall in the range 176 to 179°) (dppm = bis(diphenylphosphino)methane) [21,22],

^{*} Corresponding authors. Fax: +86 20 87112053. *E-mail address:* shzhzhan@scut.edu.cn (S. Zhan).

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Scheme 1. Generic triazene and triazenido binding modes.



Fig. 1. ORTEP view of ligand (HL). Selected bond distances (Å) and angles (°) are as follows: N(2)-N(3), 1.264(3); N(3)-N(1), 1.313(3); N(2)-C(4), 1.387(3); N(4)-C(4), 1.308(4); N(1)-N(3)-N(2), 112.8(2); N(3)-N(2)-C(4), 113.1(2); N(3)-N(1)-C(8), 121.5(2); N(4)-C(4)-N(2), 120.9(3).

the Cu–Cu–Cu unit in **1** significantly deviates from a linear arrangement $(\angle Cu(1)-Cu(2)-Cu(3) = 151.02(9)^\circ)$.

1 resides on a general position with two independent Cu–Cu distances of 2.5386(8) and 2.5983(7) Å, which are longer than those

of the triazenide copper(I) dimeric complex $[Cu(Ar-NNN-Ar)]_2$ (2.4289 Å) (Ar = o-C₆H₄-CO₂CH₃) [23], and the polypyridylamine copper(II) trinuclear complex $[Cu_3(bipyam-H)_4Cl_2]$ (2.471(1) Å) (bipyam-H = bis(2-pyridyl)amide) [24]. However, in the triazenide



Fig. 2. ORTEP view of **1**. THF and methanol molecules are omitted for clarity. Selected bond distances (Å) and angles (°) are as follows: Cu(1)–N(9), 1.967(3); Cu(1)–N(5), 1.976(3); Cu(1)–N(2), 2.006(4); Cu(1)–Cu(2), 2.5983(7); Cu(2)–N(10), 1.959(3); Cu(2)–N(6), 1.991(4); Cu(2)–N(1), 2.002(4); Cu(2)–Cu(3), 2.5386(8); Cu(3)–N(12), 1.915(4); Cu(3)–N(8), 1.929(4); C(30)–N(1), 1.319(5); C(30)–N(2), 1.346(5); Cu(1)–Cu(2)–Cu(3), 151.62(3); N(8)–Cu(3)–N(12), 165.49(15); N(6)–Cu(2)–N(10), 127.27(15); N(5)–Cu(1)–N(9), 135.08 (15); N(2)–Cu(1)–N(5), 85.64(10); N(2)–Cu(1)–N(9), 85.27(10); N(1)–Cu(2)–N(6), 127.27(15); N(1)–Cu(2)–N(10), 118.86(14).



Fig. 3. Emission spectrum of 1 in CH₃CN.

silver(I) dimer $[Ag(Ar-NNN-Ar)]_2$, the Ag–Ag distance is quite long (2.707(2) Å) [23]. This observation leads us to conclude that the triazenide ligands are not solely responsible for the M–M distances.

Compared with the structure of HL, the triazenide ligand in **1** shows a little variation of the bonding on coordination. For example, the N(2)–C(4) and N(4)–C(4) bond distances are 1.387(3) and 1.309 (4) Å, respectively. It would be expected that the N–C bond distances would be dissimilar as a consequence of the different bond order between these atoms. The corresponding bond distances (N(2)–C(30) and N(1)–C(30)) are 1.346(5) and 1.319(5) Å, respectively.

The emission spectrum of **1** in CH₃CN solution was measured at room temperature. As shown in Fig. 3, when excited upon 412 nm, **1** shows a strong band at 502 nm. It is possible that the emitting state is related to the metal-centered excited state $3d^{10}$ of Cu(I), modified by the copper–copper interaction, due to configuration mixing of the filled orbital of d parentage with the appropriate empty orbitals derived from the higher 4 s and 4p atomic orbitals of the dimeric copper unit (d–s) [25].

The electrochemical property of **1** was measured by cyclic voltammetry in CH₃CN solution. As shown in Fig. 4, CV of **1** reveals two reversible waves at -0.06 and 0.83 V, which correspond to two one-electron oxidation of Cu₃ unit ($[Cu_3]^{4+}/[Cu_3]^{3+}$), and ($[Cu_3]^{5+}/[Cu_3]^{4+}$), respectively.

In summary, the present study shows that 1-[(2-carboxymethyl) benzene]-3-[benzothiazole]triazene can support a trinuclear copper(I)



Fig. 4. Cyclic voltammogram of 1 in CH₃CN/0.1 mol L⁻¹ [Bu₄N]ClO₄ at 100 mV s⁻¹ scan rate.

cluster. Currently we are exploring this further, as well as the reactions of HL with other metals.

Acknowledgments

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Appendix A. Supplementary material

CCDC 773556 and 775010 contain the supplementary crystallographic data for triazenide ligand (HL) and complex **1**, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac. uk/conts/retrieving.html, 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. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2010.07.027.

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- [15] Synthesis of HL. A solution of methyl anthranilate (10 mmol) in water (5 ml) was mixed with 1 mol L⁻¹ HCI (30 ml, 30 mmol) at 0 °C. An aqueous solution (15%) of sodium nitrite (15 mmol) was added dropwise with stirring. Once the amine was dissolved, a 15% solution of 2-aminobenzothiazole (10 mmol) in ethanol was added at 0 °C and stirred for 6 h. The reaction mixture was neutralized with a 15% aqueous of NaCH₃CO₂ to give a yellow precipitate. The reaction mixture was filtered, and the solid was purified by crystallization at -4 °C from 9:1 ethyl acetate/hexanes to obtain yellow crystals, which were collected and dried in *vacuo* (2.16 g, 69%). Calcd for C₁sH₁₂N₄O₂S: C, 57.63; H, 3.84; N, 17.93. Found: C, 57.17; H, 3.94; N, 17.90. ¹H NMR (CDCl₃): δ 13.04 (s, 1H, N-H), 8.09 (d, J = 2.5 Hz, 1H, Ar), 7.96 (d, J = 2.8 Hz, 1H, Ar), 7.82 (d, J = 2.5 Hz, 1H, Ar), 7.47 (t, J = 5 Hz, 1H, Ar), 7.39 (t, J = 5 Hz, 1 Hz, N), 3.99 (s, 3H, -OCH₃). UV-vis [CH₃CN, λ_{max}/nm (ε/L mol⁻¹ cm⁻¹)]: 216 (1.3 × 10⁵), 260 (3.6 × 10⁴), 390 (1.1 × 10⁵).
- [16] Synthesis of 1. To a solution, containing ligand HL (0.32 g, 1.0 mmol) and triethylamine (0.10 g, 1.0 mmol) in THF/methanol (25 ml, 1:1), CuCl (0.10 g, 1.0 mmol) was added and the mixture was stirred for 1 h. The solution was allowed to slowly evaporate to afford red crystals, which were collected and dried in vacuo (0.181 g, 48.5%). Calcd for C₄₅H₃₃Cu₃N₁₂O₆S₃: C, 48.01; H, 2.93; N, 14.94. Found: C, 48.18; H, 3.07; N, 14.92. UV-vis [CH₃CN, λ_{max}/nm (ε/L mol⁻¹ cm⁻¹)]: 610 (1.2 × 10³), 379 (8.6 × 10³), 298 (2.0 × 10⁴), 234 (3.4 × 10⁴). Fluorescence spectrum: λ_{ex} = 412 nm, λ_{em} = 502 nm.
 [17] Crystal data for HL: C₁₅H₁₂N₄O₂S, monoclinic, space group P2(1)/n, a = 8.8944
- [17] Crystal data for HL: $C_{15}H_{12}N_4O_2S$, monoclinic, space group P2(1)/n, a=8.8944(18), b=13.475(3), c=12.329(3) Å, $\alpha=90$, $\beta=92.49(3)$, $\gamma=90^{\circ}$, Z=4, ρ $c_{alcd}=1.405$ g cm⁻³, F(000)=648, R1 (wR2) = 0.0652 (0.1999) ($l>2\sigma(l)$), R1 (wR2) = 0.0892 (0.2131) (all data), GOF = 1.099
- [18] Crystal data for 1 THF CH₃OH: $C_{50}H_{45}Cu_3N_{12}O_8S_3$, triclinc, space group P-1, a = 13.813(2), b = 14.407(2), c = 15.304(2) Å, $\alpha = 116.840(2), \beta = 105.563(2), c = 15.304(2)$ Å, $\alpha = 116.840(2), \beta = 105.563(2), c = 15.304(2)$

$$\begin{split} &\gamma \!=\! 94.139(2)^{\circ}, \ Z \!=\! 2, \ \rho_{calcd} \!=\! 1.6 \ \text{g cm}^{-3}, \ F(000) \!=\! 1256, \ R1 \ (wR2) \!=\! 0.0520 \\ &(0.1366) \ (l\!>\! 2\sigma(l)), R1 \ (wR2) \!=\! 0.0920 \ (0.1644) \ (all \ data), \ GOF \!=\! 1.014. \ -\!\!\!> \\ &[19] \ J.G. \ Rodriguez, \ M. \ Parra-Hake, \ G. \ Aguirre, \ F. \ Ortega, \ P.J. \ Walsh, \ Polyhedron \ 18 \end{split}$$

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