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Multiple metal coordinating behaviour of the tetrapodal ligand 1,1,1,1-tetrakis [(salicylaldimino)methyl]methane

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ABSTRACT

The tetrapodal ligand 1,1,1,1-tetrakis[(salicylaldimino)methyl]methane (H₄tsam) has been introduced for the first time for metal complexation. Two zinc(II) complexes[Zn₂(tsam)] (1) and [Zn₃(Htsam)₂]·2C₇H₈ (2) have been obtained by reacting zinc acetylacetonate with the ligand in the presence of triethylamine, while a cobalt(III) complex [Co(Htsam)]·CH₃CN·H₂O (3) is obtained when Co(ClO₄)₂·6H₂O is reacted in air. All the compounds have been characterized by their elemental analyses and ESI-MS, IR, UV-VIS and ¹H NMR spectra. The X-ray crystal structures of H₄tsam, 2 and 3 have been determined. Compounds **1** and **2** exhibit fluorescence in solution and the lifetimes of their luminescence decay have been measured. Thermal analysis (TGA, DTA) of 2 with regard to loss of encapsulated toluenes and redox behaviour of 3 have been studied. © 2010 Elsevier B.V. All rights reserved.

The role of topology is quintessential for polypodal ligands in controlling structure, stereochemistry and reactivities of their metal complexes [1]. Tripodal ligands, in which boron [2], nitrogen [3], phosphorous [2], or carbon [4] acts as the ligand bridge head, have extensive coordination chemistry that range from structural and functional modeling of metalloenzymes [5] to molecular magnetism [6,7]. Although the chemistry of tetrapodal ligand metal complexes is relatively less widespread [8], they find important applications, inter alia, as medical diagnostic probes e.g. MRI contrast agents [9], and chemotherapeutic agents [10]. Unlike tripodal ligands which have a single atom as the bridge head, tetrapodal ligands used for metal complexation have more than one bridge heads. In our effort to explore the metal complex chemistry of tetrapodal ligands with a single bridge head, we have designed a number of ligands by derivatizing 1,1,1,1-tetrakis(2-aminomethyl)methane. Herein we report the synthesis, structure and physico-chemical properties of 1,1,1,1-tetrakis[(salicylaldimino)methyl]methane (H₄tsam) and its zinc(II) and cobalt(III) complexes.

The hydrochloride salt of 1,1,1,1-tetrakis(2-aminomethyl)methane $C(CH_2NH_2)_4 \cdot 4HCl$ was prepared by modification of a procedure reported in literature[11] from pentaerythritol in 45% overall yield following the protocols outlined in Scheme 1. The ligand H₄tsam was obtained in 80% yield by reacting $C(CH_2NH_2)_4 \cdot 4HCl$, $N(C_2H_5)_3$ and salicylaldehyde in 1:4:4 molar ratio in methanol [12]. The ball and stick representation of H₄tsam, which crystallizes with the monoclinic space group C2/c (Z=4) [13], is shown in Fig. 1. The average values of the C–C–C angles around the central carbon C(9) is 109.7 \pm 1.1°. All the phenolic protons are strongly hydrogen-bonded to their adjacent imine nitrogens with average O····N distances and O–H····N angles being 2.601(4) Å and 146.9(1)°, respectively.

In a reaction involving three equivalents of zinc acetylacetonate, two equivalents H₄tsam and six equivalents of N(C₂H₅)₃ in boiling acetonitrile, a yellow product that precipitated out during reflux was found to have the composition $[Zn_2(tsam)]$ (1) [14]. This compound was previously obtained in a different way [11]. A second product was isolated from the filtrate first by evaporating it to dryness, followed by extraction with benzene and finally with addition of toluene to the hot benzene concentrate $[Zn_3(Htsam)_2] \cdot 2C_7H_8$ (2) [15] separated out as light yellow crystals. The relative yield of the two products was ca. 60% (1) and 25% (2). However, when the above reaction was carried with the reactants in the molar ratio 2:1:4, compound 1 was isolated as the sole product in 90% yield. Compounds 1 and 2 have been characterized by their elemental (C, H and N) analysis, ESI-MS, IR and ¹H NMR spectra. The strongest peak observed in the ESI-MS at m/z = 676 for 1 and 1286.5 for **2** correspond to ions $[Zn_2(tsam) + H]^+$ and $[Zn_3]$ $(Htsam)_2 + H]^+$, respectively. As shown in Fig. 2, the observed and simulated isotopic distribution patterns for both of the cationic species $[1 + H]^+$ and $[2 + H]^+$ are in excellent agreement with each other. Because of poor solubility of 1, diffraction quality crystal of the compound could not be obtained. Nevertheless, the composition and the spectroscopic data of [Zn₂(tsam)] indicate that each of the metal centers are coordinated to two salicylaldimine units symmetrically to obtain ZnN₂O₂ coordination sphere.

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Scheme 1.

The perspective structural view of $[Zn_3(Htsam)_2]$ in **2** [16] (Fig. 3a) shows that out of four salicylaldimines of H₄tsam only three are involved in metal coordination. In the trinuclear core N₃Zn(μ -O₃)Zn



Fig. 1. Ball and stick representation of H₄tsam. Selected bond parameters: C(8)-C(9) = 1.531(2), C(9)-C(10) = 1.529(2), N(1)-C(7) = 1.265(2), N(1)-C(8) = 1.459(2), N(2)-C(10) = 1.457(3), N(2)-C(11) = 1.276(2), O(1)-C(1) = 1.348(2), O(2)-C(17) = 1.350(2)Å, C(10)-C(9)-C(8) = 109.41(10), C(10)#1 – C(9)-C(10) = 110.80(2), C(10)#1–C(9)-C(8) = 108.46(10), C(8)-C(9)-C(8)#1 = 110.3(2)°. Symmetry transformations used to generate equivalent atoms: (-x + 1), $y_1(-z + \frac{1}{2})$.

 $(\mu$ -O₃)ZnN₃, the crystallographically equivalent terminal metal centers [Zn(1)/Zn(1')] are coordinated to three imine nitrogens and three phenolate oxygens of three pendant salicylaldimines, while the central metal Zn(2) obtains ZnO₆ coordination sphere as all the phenolate oxygens act as bridges. Fig. 3b shows the coordination polyhedra that resulted due to the sharing of the O₃ faces of the terminal and central metal atoms. In the terminal ZnN₃O₃ coordination sphere, the average value of the largest N–Zn (1/1')–O angles [154.5(9)°] indicates its significant distortion from regular octahedral geometry. On the other hand, for the central Zn(2), all the three trans O–Zn(2)–O angles are 180°. A closer look of the trigonal planes of the terminal metal centers reveals that they are prismatically twisted.

Consideration of the Zn(2)–O bond distances indicate that relative to the four identical equatorial Zn(2)–O(1/1', 2/2') bonds [2.096(5)Å], the two axial Zn(2)–O(3/3') bond [2.149(5)Å] is longer. Clearly, Zn(2) has an axially elongated octahedral geometry (D_{4h}). The extent of trigonal prismatic distortion is given by the twist angle ϕ [17], which is 0° for perfect trigonal prism (D_{3h}) and 60° for both trigonal antiprism (D_{3d}) and octahedron (O_h). The average value of ϕ for Zn(1/1') turns out to be 27.6°, which indicates that the distortion from regular octahedron to trigonal prism is 54% complete. Further, the N₃ and O₃ trigonal planes are practically parallel to each other (their dihedral angle is 0.28°) and the distance between the centroids of the two planes is 2.748Å. The intermetallic Zn(1)–Zn(2)–Zn(1') axis is perfectly linear, while the distance between two adjacent metals Zn(1/1')·····Zn(2) is 2.913(4)Å.

The stereochemical configuration of the terminal metal centers of the complex, as obtained by viewing the orientations of the three



Fig. 2. ESI-MS of complexes 1 and 2 showing observed and simulated isotopic abundance patterns for the most strong peaks.



Fig. 3. (a) Perspective representation of $[Zn_3(Htsam)_2] \cdot 2C_7H_8$ (2). Selected bond parameters: Zn(1) - O(1) = 2.094(4), Zn(1) - O(2) = 2.107(5), Zn(1) - O(3) = 2.124(4), Zn(1) - N(1) = 2.096(6), Zn(1) - N(2) = 2.101(6), Zn(1) - N(3) = 2.116(6), Zn(2) - O(1) = 2.096(4), Zn(2) - O(2) = 2.096(5), Zn(2) - O(3) = 2.149(5), $Zn(1/1') \cdots Zn(2) = 2.913(4)$ Å: O(1) - Zn(1) - N(3) = 155.3 (2), O(2) - Zn(1) - N(1) = 153.3(2), O(3) - Zn(1) - N(2) = 154.81(19), $O(1) - Zn(2) - O(1) \# 1 = 180.0^\circ$ °. Symmetry transformations used to generate equivalent atoms: (-x + 2), (-y + 1), -z. (b). Coordination polyhedra of $[Zn_3(Htsam)_2] \cdot 2C_7H_8$. (c). Homochiral ($\Delta - \Delta$) configuration of $[Zn_3(Htsam)_2] \cdot 2C_7H_8$. (d). Packing diagram showing hydrogen bonds and short contacts in $[Zn_3(Htsam)_2] \cdot 2C_7H_8$ (2).

chelate rings $\dot{N} - C - C - C - O - Zn$ along the intermetallic axis (Fig. 3c), is homochiral $\Delta - \Delta$ (or $\Lambda - \Lambda$). Moreover, all the three sixmembered $\dot{N} - C - C - C - N - Zn$ rings have the twisted boat conformation $\delta\delta\delta$. Since compound **2** has a centrosymmetric space group (P-1), it crystallizes in racemic form.

The packing diagram of [Zn₃(Htsam)₂]·2C₇H₈ (Fig. 3d) viewed along [001] plane shows that the toluenes are trapped between two layers of complex molecules. As may be noted in Fig. 3d, the C(102)-H proton of toluene is involved in weak intermolecular hydrogen bonding with the oxygen atom O(4) of the uncoordinated salicylaldimine moiety and the $C(102) \cdots O(4)$ distance is 3.52 Å. Again, in the uncoordinated salicylaldimine, the phenolic O-H and imine nitrogen are intramolecularly hydrogen-bonded with $O(4) \cdots N(4)$ distance being 2.574 Å and $\angle O(4)$ -H····N(4) is 147°.

The thermal stability of 2 with regard to the loss of encapsulated solvent molecules has been studied by thermogravimetric and differential thermal analyses. Fig. 4 shows that onset of desolvation takes place at 140°C and completes at 220°C. The observed weight loss 12.35% is in agreement with the value 12.53% expected for the loss of two toluene molecules from 2.

The absorption and emission spectra of compounds 1 and 2 in dimethyl sulfoxide and acetonitrile respectively are shown in Fig. 5. The absorption maxima of the compounds are located at 366 nm for 1 $(\epsilon = 23,000 \text{ M}^{-1} \text{ cm}^{-1})$ and at 353 nm for **2** ($\epsilon = 25,500 \text{ M}^{-1} \text{ cm}^{-1}$). The two compounds also exhibit a second more intense band (not shown in Fig. 5) at 265 nm (ϵ =57,000 M⁻¹ cm⁻¹) for **1** and 258 nm $(\epsilon = 59,000 \text{ M}^{-1} \text{ cm}^{-1})$ for **2**. It appears that the higher energy stronger band is due to π - π ^{*} transition of the aromatic rings, while the lower energy band is due to $C = N \pi - \pi^*$ transition. Although the ligand itself does not show any luminescence spectrum at room temperature, both 1 and $\mathbf{2}$ exhibit strong luminescence when their C = N absorption bands are excited. In the case of 1, the luminescence peak occurs at 450 nm, while for **2** this peak is observed at 440 nm.

It may be noted that the relative intensities of the luminescent band of the two compounds bear similar relationship to their absorbance intensities. The Stokes' shift $(\overline{V}_{abs} - \overline{V}_{em})^{T}$ of the compounds, 5100 cm⁻¹ (1) and 5600 cm⁻¹ (2), are also of comparable energies. The time resolved photoluminescence decay of 1 (in dimethyl sulfoxide) and **2** (in acetonitrile) are shown in Fig. 6. The lifetime (τ) values obtained by analyzing single exponential decay curves are practically same for **1** (13.10 ± 0.10 ns) and **2** (13.20 ± 0.23 ns). The quantum yield (ϕ) of **1** (in dimethyl sulfoxide) is 0.22, while that of **2** (in acetonitrile) is 0.26.

The reaction between $Co(ClO_4)_2 \cdot 6H_2O$ and H_4 tsam in the presence of $N(C_2H_5)_3$ in air led to the isolation of the cobalt(III) complex $[Co(Htsam)] \cdot CH_3CN \cdot H_2O(3)$ [18]. The ¹H NMR spectrum of 3 indicates the involvement of three salicylaldimine units of the



100 0.0 0 350 450 500 550 300 400 600 650 Wavelength / nm

Fig. 5. Absorption and emission profiles of [Zn₂(tsam)] (1) (bold line) in dimethyl sulfoxide and $[Zn_3(Htsam)_2] \cdot 2C_7H_8(2)$ (dotted line) in acetonitrile.

ligand in the metal chelation and the spectator role of the fourth one. On the other hand, the ESI-MS of 3 indicates the occurrence of unipositive monomeric as well as dimeric cations in the plasma. As shown in Fig. 7, in methanol, three peaks due to $[Co(Htsam) + H]^+$ (m/z = 605.37, 12%), $[Co(Htsam) + Na]^+$ (m/z = 627.37, 100%) and $[{Co(Htsam)}_2 + Na]^+ (m/z = 1231.75, 10\%)$ are observed, whereas in acetonitrile, the relative abundances of the peaks due to [Co $(Htsam) + H]^+$ (m/z = 604.90), $[Co(Htsam) + Na]^+$ (m/z = 626.89)and $[{Co(Htsam)}_2 + H]^+$ (m/z = 1208.58) are 100%, 10% and 15%, respectively. The observation of the dimerized cationic species is intriguing.

A plausible explanation could be the uncoordinated phenolic OH of **3** in the ESI-MS condition undergoes dimerization as:



Complex **3** is further characterized by the observation of two bands at 400 and 550 nm in the visible region of the absorption spectrum. which can be attributed to ${}^{1}A_{1g} \rightarrow {}^{1}T_{2g}$ and ${}^{1}T_{1g}$ transitions, respectively. Further, the compound undergoes quasi-reversible reduction in acetonitrile with $E_{1/2} = -890$ mV and $\Delta E_p = 140$ mV at a scan rate of 100 mV s⁻¹.

The X-ray structure of 3 [19] (Fig. 8) shows a near perfect octahedral geometry for the [CoN₃O₃] coordination sphere. All the Co–O and Co–N distances are almost equal $(1.90 \pm 0.01 \text{ Å})$, as are the three O–Co–N trans angles $(178 \pm 1^{\circ})$. Similar to **2**, in this case also $O(4) \cdots N(4)$ distance is 2.60 Å and O(4)-H····N(4) angle is 146.1°.

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Appendix A. Supplementary material

CCDC 775643-775645 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data_request/cif.

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- [12] Anal. Calcd for C₃₃H₃₂N₄O₄: C, 72.26; H, 5.84; N, 10.21. Found: C, 72.20; H, 5.79; N, 10.17. IR (KBr, ν/cm^{-1}): 1631 ($\nu_{C=N}$). ¹H NMR (300 MHz, CDCl₃) δ/ppm 13.22 (s, 4H, PhOH); 8.43 (s, 4H, CH = N); 7.34 (t, 4H, J₁ = 8.54 Hz, J₂ = 8.53 Hz, Ar); 7.25 (d, 4H, J = 9.05 Hz, Ar); 6.98 (d, 4H, J = 8.23 Hz, Ar); 6.90 (t, 4H, $J_1 = 7.53$ Hz, J₂ = 7.28 Hz, Ar); 3.78 (s, 8H, CH₂)
- [13] H₄tsam: $C_{33}H_{32}N_4O_4$, M = 548.63, colourless needle, Monoclinic, space group C2/c, a = 17.143(2), b = 11.2269(14), c = 15.689(2)Å, $\beta = 105.965(3)^{\circ}$,



Fig. 6. Steady state decay profiles of [Zn₂(tsam)] (1) (a) and [Zn₃(Htsam)₂]·2C₇H₈ (2) (b) in dimethyl sulfoxide and acetonitrile respectively.



Fig. 6 (continued).

U = 2903.0(6) Å³, Z = 4, D_c = 1.255 Mg m⁻³, μ (Mo-Kα) = 0.084 mm⁻¹, T = 123(2) K, F(000) = 1160, h, k, l limiting indices: -22 <=h <=22, -14<=k <=14, -20 <=1 <=20, crystal size/mm³ = 0.40 x 0.10 x 0.08, no. of data = 3339, restrains = 0, params = 188, no.of reflns [I>2σ (I)] = 3339, gof = 0.834, final R indices[I>2σ (I)]: R1 = 0.0425, wR2 = 0.0820, R indices (all data): R1 = 0.1098, wR2 = 0.0980.

- [14] Anal. Calcd for $C_{33}H_{28}N_{40}A_{71}c_{...}$ (5.8.67; H, 4.15; N, 8.29. Found: C, 58.55; H, 4.20; N, 8.25. FT-IR (KBr, v/cm⁻¹): 3202(w), 2902 (w), 1627 (s), 2598 (m), 1542 (m), 1471 (m), 1448 (m), 1402 (w), 1317 (m), 1195 (m), 1153 (w), 796 (w), 756 (m), 588 (w). ESI-MS (positive) in CH₃CN: m/z=676 [Zn₂(tsam) + H]⁺ (100%). ¹H NMR (300 MHz, (CD₃)₂SO) δ /ppm 8.12 (s, 4H, CH = N); 7.13 (t, 4H, J₁ = 6.93 Hz, J₂ = 7.01 Hz, Ar); 7.01 (d, 4H, J = 7.61 Hz, Ar); 6.58 (d, 4H, J = 8.41 Hz, Ar); 6.37 (t, 4H, J₁ = 7.13 Hz, J₂ = 7.22 Hz, Ar); 3.59 (s, 8H, CH₂) [15] Anal. Calcd for C₈₀H₇₄N₈O₈Zn₃: C, 65.28; H, 5.03; N, 7.61. Found: C, 65.40; H, 5.13; N, 7.55. FT-IR (KBr, v/cm⁻¹): 3464 (w, br), 2891 (w), 1630 (s), 1599 (w), 1543

indices [I>2 σ (I)]: R1=0.0616, wR2=0.0843, R indices (all data): R1=0.2056, wR2=0.1240

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- [18] Anal. Calcd for $C_{33}H_{34}N_5O_5Co: C, 63.29; H, 5.12; N, 10.54. Found: C, 63.23; H, 5.07; N, 10.60. ESI-MS (positive) in CH₃OH: m/z = 605.37 [Co(Htsam) + H]⁺ (12%), 627.37 [Co(Htsam) + Na]⁺ (100%), 1231.75 [{Co(Htsam)}_2 + Na]⁺ (10%). ESI-MS (positive) in CH₃CN: 604.90 [Co(Htsam) + H]⁺ (100%), 626.89 [Co(Htsam) + Na]⁺ (10%), 1208.58 [{Co(Htsam)}_2 + H]⁺ (15%). FT-IR (KBr, v) cm⁻¹): 3446 (m, br), 1626 (s), 1601 (s), 1537 (m), 1468 (m), 1448 (s), 1396 (w), 1352 (w), 1321 (m), 1205 (m), 1151 (m), 1027 (w), 904 (w), 758 (m), 617 (w). ¹H NMR (300 MHz, CDCl₃): <math>\delta$ /ppm 12.46 (s, 1H, Ar-OH); 8.47 (s, 4H, CH = N); 7.47 (s, 4H, Ar-H); 7.13 (t, 4H, J = 7.82 Hz, Ar-H); 7.03 (d, 4H, J = 7.50 Hz, Ar-H); 6.45 (t, 4H, J = 7.28 Hz, Ar-H); 3.94 (d, 3H, J = 12.60 Hz, coordinated CH₂ (ax/eq)); 3.31 (d, 3H, J = 12.42 Hz, coordinated CH₂
- $\begin{array}{l} \label{eq:space-$



Fig. 7. ESI-MS spectra of [Co^{III}(Htsam)] (3) in CH₃OH (a) and CH₃CN (b).



Fig. 8. Ball and stick representation of $[Co^{III}(Htsam)]$ -CH₃CN·H₂O (**3**) Selected bond parameters: Co-N(1) = 1.905(3), Co-N(2) = 1.909(2), Co-N(3) = 1.899(2), Co-O(1) = 1.910(19), Co-O(2) = 1.893(2), Co-O(3) = 1.886(19)Å; N(1)-Co-O(1) = 92.31(9), N(1)-Co-O(2) = 176.73(9), N(1)-Co-O(3) = 91.10(9), N(2)-Co-O(1) = 89.97(9), N(2)-Co-O(2) = 93.09(10), N(2)-Co-O(3) = 176.48(9), N(3)-Co-O(1) = 178.91(9), N(3)-Co-O(2) = 90.15(9), N(3)-Co-O(3) = 94.20(9), N(1)-Co-N(2) = 89.82(10), N(1)-Co-N(3) = 88.41(10), N(2)-Co-N(3) = 89.22(10), O(1)-Co-O(2) = 89.17(9), O(1)-Co-O(3) = 86.60(8), O(2)-Co-O(3) = 86.68(9)^\circ. Water of crystallization is shown as O(100).