**Synthesis and Structural Elucidation of a Novel Hetero-Dodecametallic Yttrium-Sodium Complex Based on EDTA: Insights into f/s-Block Coordination Chemistry**

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**ABSTRACT**

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| Heterometallic f/s-block complexes are not plentiful but play pivotal roles in understanding metal synergy in materials science and catalysis. Reaction of Y(NO3)3.6H2O with EDTANa2.2H2O (ethylenediaminetetraacetic acid, disodium salt dihydrate) gives the dodecanuclear {Y4Na8(*L*)4(OH)2(NO3)2(H2O)16} (**1**). Complex (**1**) is characterized by elemental analyses, IR and conductance measurement. The structure of (**1**) was elucidated by X-ray diffraction analysis. The compound crystallizes in the monoclinic space group P21/c with the following parameters: *a* = 24.81289 (15) Å, *b* = 15.63590 (8) Å, *c* = 19.68764 (14) Å, **= 106.6623 (7)°, *V* = 7317.53 (8) Å3, *Z*= 4, *R*1= 0.041, *wR*2 = 0.117. The asymmetric unit of the compound contains four tetradeprotonated (*L*4-) EDTA molecules, four octacoordinated yttrium ions, three pentacoordinated sodium ions, five hexacoordinated sodium ions, two chelating nitrate groups, two hydroxy groups acting in μ2-mode, seven coordinated water molecules acting in η1-mode and nine coordinated water molecules acting in μ2-mode. Each of the YIII cations is coordinated by one fully deprotonated EDTA which link also four NaI cations. Each of the NO3- anions bridge two YIII ions, while each of the two hydroxy groups bride one YIII cation and one NaI cation. The environment around the octacoordinated YIII cations are best described as a square antiprisms. The environments around the pentacoordinated NaI ions are best described as a square pyramidal geometries, while the hexacoordinated NaI ions exhibit octahedral environments. The molecule features a typical 3D hydrogen-bonded network with diverse coordination geometries (square antiprismatic Y³⁺, square pyramidal/octahedral Na⁺). |

*Keywords: Yttrium, EDTA, Sodium, Square antiprism, Square pyramidal, Octahedral*

# Introduction

Coordination chemistry combining elements of the "f" and "s" block is of increasing interest to chemists because of their original structures 1–4, and their interesting properties in various fields such as magnetism 5, catalysis 6, fluorescence 7. The main procedure used to synthesize these types of complexes is the self-assembly method. Ligands possessing several arms with multiple coordination sites can be considered as structural and functional analogues of crown ethers which are among the first precursors used to carry out self-assembly reactions in solution to form coordination complexes with multiple metal centers. It is possible to synthesize not only homo-polymetallic complexes, but also hetero-polymetallic complexes by single-step reactions 8. The controlled formation of supramolecular coordination complexes containing several types of metals remains a synthetic challenge 9,10. Although crown ethers, cryptands, and related ligands are effective groups of compounds for complexing alkali ions with other types of 3d or 4f metals, many simpler and cheaper ligands are available that allow complexes combining s/d, s/f, d/d, or d/f ions 11–16. These ligands include N,N'-bis(3-methoxysalicylidene)-propane-1,3-diamine 17, 3-ethoxysalicylaldehyde-diamine 11,13, 2-(-(2-(-2-hydroxy-3-methoxybenzylideneamino)phenylimino)methyl)-6-methoxyphenol 18. These compartmentalized Schiff bases have already been used to prepare various heterobimetallic complexes 19–22. Many such complexes exhibit important properties such as magnetism 21,22, luminescence 23,24 and medical applications 25. In the present work, we used a cheap ligand, EDTANa2.2H2O (ethylenediaminetetraacetic acid, disodium salt dihydrate), to prepare a hetero-dodecametallic complex, {Y4Na8(L)4(OH)2(NO3)2(H2O)16}, where the four yttrium(III) atoms have a square antiprism geometry and where three of the sodium atoms are in a square pyramid environment and five sodium atoms have an octahedral geometry.

# Material and methods

## Starting materials and methods

All chemicals and solvents were of analytical reagent grade and were used directly without further purification. Elemental analyses of C, H and N were recorded on a VxRio EL Instrument. Infrared spectra were obtained on a FTIR Spectrum Two of Perkin Elmer spectrometer in the 4000-400 cm-1 region. The molar conductance of 1×10-3 M in DMF solutions of the metal complex was measured at 25 °C using a WTW LF-330 conductivity meter with a WTW conductivity cell.

## Synthesis of complex {Y4Na8(*L*)4(OH)2(NO3)2(H2O)16} (1)

Y(NO3)3.6H2O (0.3830 g, 1 mmol) was dissolved in methanol (10 mL). Ethylenediaminetetraacetic acid, disodium salt dihydrate (EDTANa2.2H2O) (0.3722 g, 1 mmol) was dissolved in 10 mL of methanol and NaOH (0.08 g, 2 mmol) was added. The two solutions were mixed and refluxed under stirring for 60 minutes. On cooling, the purple solution was filtered, and the filtrate was left for slow evaporation. After one week, purple crystals suitable for X-ray analyses were collected. Analysis calculated for [C40H82N10O56Na8Y4] C, 22.44; H, 3.84; N, 6.52. Found: C, 22.46; H, 3.86; N, 6.55. FTIR (ν, cm-1) : 3220, 1584, 1515, 1392, 1331, 1253, 1095, 1040, 931, 842. 5–8 S.cm2.mol-1.

## Crystal Structure Determination

Crystals suitable for single-crystal X-ray diffraction, of the reported compound (1), were grown by slow evaporation of MeOH solution of the complex. Details of the crystal structure solution and refinement are given in Table 1. Diffraction data were collected using a Rigaku FRE+ equipped with Varimax confocal mirrors and UG2 Universal goniometer with graphite monochromatized CuKα radiation (λ = 1.54184 Å). All data were corrected for Lorentz and polarization effects. Complex scattering factors were taken from the program package SHELXTL 26. The structures were solved by direct methods which revealed the position of all non-hydrogen atoms. All the structures were refined on *F2* by a full-matrix least-squares procedure using anisotropic displacement parameters for all non-hydrogen atoms 27. H atoms (CH2 groups) were geometrically optimized and refined as riding models by AFIX instructions. Molecular graphics were generated using ORTEP 28.

**Table 1: Crystal data, X-ray data collection, data reduction and structure refinement for 1.**

|  |  |
| --- | --- |
| Chemical formula | C40H82N10Na8O56Y4 |
| *M*r | 2138.71 |
| Crystal system | Monoclinic |
| Space group | *P*21/*c* |
| Temperature (K) | 100 |
| *a* (Å) | 24.81289 (15) |
| *b* (Å) | 15.63590 (8) |
| *c* (Å) | 19.68764 (14) |
| β (°) | 106.6623 (7) |
| *V* (Å3) | 7317.53 (8) |
| *Z* | 4 |
| Radiation type | Cu *K*α |
| µ (mm−1) | 5.73 |
| Crystal size (mm) | 0.25 × 0.2 × 0.15 |
| *T*min, *T*max | 0.634, 1.000 |
| No. of measured, | 102549 |
| independent | 15739 |
| observed [*I* > 2σ[(](https://d.docs.live.net/8584039BB42D259F/Bureau/PUB%20Ndioga%202025/20220914nf11c_auto%20_reflns_threshold_expression)*I*[)](https://d.docs.live.net/8584039BB42D259F/Bureau/PUB%20Ndioga%202025/20220914nf11c_auto%20_reflns_threshold_expression)] reflections | 14020 |
| *R*int | 0.041 |
| *R*[*F*2 > 2σ(*F*2)] | 0.040 |
| *wR*(*F*2) | 0.117 |
| GOF on-fit | 1.07 |
| No. of reflections | 15739 |
| No. of parameters | 1171 |
| No. of restraints | 19 |
| Δρmax, Δρmin (e Å−3) | 1.96, −1.28 |

# Results and discussion

### General Studies

Reaction of Y(NO3)3.6H2O and H2*L*Na2 (ethylenediaminetetraacetic acid, disodium salt dihydrate) in presence of sodium hydroxide produces the heterododecanuclear complex formulated as {Y4Na8(*L*)4(OH)2(NO3)2(H2O)16}. The results of the elemental analyses agree with the proposed formula. The infrared spectra of the ligand and the complex show bands characteristic of the functions of the ligand and those relating to water molecules. Among the vibrations of the free ligand, we present those due to functions involved in the complexation through the donor atoms such. The vibrations relative to νas(C=O) and νs(C=O) appear, respectively, at 1615 cm-1 and 1393 cm-1 for the ligand. Upon coordination of the ligand with metal atoms these bands are pointed at 1583 cm-1 and 1424 cm-1, respectively. We notice a strong shift for the band due to νas(C=O), indicating the involvement of the carbonyl oxygen atom in the coordination with metal center. The difference between νas and νs is 159 cm-1, indicating that the carboxyl groups are coordinated to the central metal ion by chelate and bidentate bridging modes 29. In the spectra of the complex the bands at *ca*. 3220 and 842 cm-1 are characteristic of coordinated water molecules 30. Molar conductivities were measured for freshly prepared solutions in DMF and after standing for two weeks. The value of the conductivity increased very slightly with time in DMF. The molar conductance value lies in the range observed for neutral electrolyte Λ = 5 S.cm2.mol-1 for fresh DMF solution and Λ = 8 S.cm2.mol-1 two weeks later for the same solution indicating a very slight dissociation in DMF solution 31.

|  |  |
| --- | --- |
|  |  |

η2, η1, η1, η2, η1, η1, η1, η1: μ5 η2, η1, η2, η2, η1, η1, η1, η1: μ5

**Figure 1. Coordination modes of the fully deprotonated ligand *L*4- as found from the crystal structure of the dodecanuclear complex.**

### X-ray structure of complex 1

The dodecanuclear complex {Y4Na8(*L*)4(OH)2(NO3)2(H2O)16} (**1**) is the result of self-assembly reaction between the equimolecular amount of Y(NO3)3.6H2O and EDTANa2.2H2O followed by addition of NaOH which acts as base for total deprotonation of the ethylenediaminetetraacetic disodium salt. The source of the Na+ cation are ensured by the sodium hydroxide and the EDTANa2.2H2O. The yielded complex (**1**) crystallizes in the monoclinic system P21/c space group. The asymmetric unit contains four Y3+ cations, eight Na+ cations, four fully *L*4- tetradeprotonated EDTA ligands, two NO3- nitrate groups, two OH- units and sixteen coordinated water molecules. Two of the *L*4- ligands coordinated in a η2, η1, η1, η2, η1, η1, η1, η1: μ5 mode bridging one Y3+ and four Na+ while two of the *L*4- ligands coordinate in a η2, η1, η2, η2, η1, η1, η1, η1: μ5 fashion bridging one Y3+ and four Na+ (Figure 1) The molecular structure and atom labeling scheme is shown in Figure 2. The four Y3+ cations are octacoordinated and are situated in a N2O6 environment. The coordination environment of Y1 ion is composed of two amino nitrogen atom and four oxygen atoms from the ligand and two oxygen atom from the nitrate anion which acts in η1, η1 mode with respect to Y1 (Figure 3a). The nitrate anion acts in η1 mode with respect to Y2 and bridge this one to Y1 (Figure 3b). The *L*4- ligand around Y1 bridge this one to four Na+ cations and two oxygen atoms of the ligand remain uncoordinated. The same observations are done for Y3 and Y4 (Figures 3c and 3d). The coordination spheres of Y3+ ions are best described as distorted square antiprism (Figure 4).

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**Figure 2 : *ORTEP* Plot (30% probability ellipsoids) showing the structure of the binuclear complex 1.**

**Table 2 : Selected bond lengths (Å) and angles (°) for the complex 1.**

|  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Y2—O24 | 2.3139 (18) | | Y3—O17 | | 2.3091 (18) | Y1—O30i | | 2.3071 (18) | | Y4—O81 | 2.3065 (18) |
| Y2—O12 | 2.3158 (18) | | Y3—O21 | | 2.3528 (19) | Y1—O3 | | 2.3460 (19) | | Y4—O34 | 2.3301 (18) |
| Y2—O25 | 2.3270 (18) | | Y3—N6 | | 2.515 (2) | Y1—N2 | | 2.505 (2) | | Y4—O28 | 2.3426 (18) |
| Y2—O11 | 2.3256 (18) | | Y3—O38ii | | 2.3374 (19) | Y1—N1 | | 2.581 (2) | | Y4—N10 | 2.572 (2) |
| Y2—N4 | 2.571 (2) | | Y3—N7 | | 2.588 (2) | Y3—O19 | | 2.2873 (19) | | Y4—N9 | 2.582 (2) |
| Y1—O6 | 2.2874 (19) | | Y3—N8ii | | 2.763 (3) | Y3—O37ii | | 2.3301 (19) | | Na4—O1A | 2.637 (2) |
| Y1—O1 | 2.3119 (19) | | Y4—O33 | | 2.3047 (19) | Y3—O18 | | 2.3246 (19) | | Na5—O1B | 2.544 (3) |
| N5—Y2—N4 | | 69.67 (7) | | Y2—O1A—Na4 | | | 124.42 (9) | | O14—Na1—O12Wiii | | 146.40 (8) |
| N2—Y1—N1 | | 69.67 (7) | | N6—Y3—N7 | | | 69.26 (7) | | O15—Na1—O30iii | | 159.51 (8) |
| O13W—Na1—O14W | | 172.04 (9) | | N10—Y4—N9 | | | 69.01 (7) | | Y4—O1B—Na5 | | 127.62 (9) |

Symmetry codes: (i) −*x*, −*y*+1, −*z*; (ii) −*x*+1, −*y*+1, −*z*+1; (iii) *x*+1, *y*, *z*.

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**a b**

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**c d**

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**e f**

**Figure 3. Coordination around Y1, Y2, Y3 and Y4.**

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**Figure 4. Plot showing the coordination spheres in the crystal : (a) pentacoordinated Na+, (b) hexacoordinated Na+ and (c) octacoordinated Y3+ in the dodecanuclear compound.**

The coordination environment of Y2 ion is composed of two amino nitrogen atom and four oxygen atoms from the ligand and one oxygen atom from the nitrate anion which acts in η1 mode with respect to Y2, one hydroxide oxygen atom which acts in μ2-mode bridge Y2 and Na4. The *L*4- ligand around Y2 bridge this one to four Na+ cations and two oxygen atoms of the ligand remain uncoordinated. As shown in Figures 3a and 3b the *L*4- molecules coordinate in different modes around Y1 and Y2. The nitrate anion acts in η1, η1 mode with respect to Y1 and bridge this one to Y2 in η1 mode. The coordination sphere of Y2 is best described as distorted square antiprism (Figure 4). The environmental coordination of Y3 and Y4 atoms are rigorously identical to the environment coordination of Y1 and Y2, respectively (Figures 3c and 3d). Upon coordination to the Y3+ each ligand form one five-membered ring of type NCCNY with bite angle of 69.67(8)° [N1—Y1—N2], 69.67(7)° [N4—Y2—N5], 69.26(7)° [N6—Y3—N7] and 69.01(7)° [N9—Y4—N10] and four five-membered ring of type NCCOY with bite angle values in the range [65.78(7)° - 70.87 (7)°].

Three of the eight sodium ions are pentacoordinated in O5 site (Figure 3e) while the five other are hexacoordinated and occupied an O6 coordination site (Figure 3f). The environment around each of the pentacoordinated sodium atom is determined using the Addison 32 parameter (τ) which is calculated with the following formula **τ**= (α- β) / 60 (where αand βare the values of the largest bond angles around the iron atom). When **τ**= 0, the geometry is a pyramid with a perfect square base; τ= 1 indicates a perfect trigonal bipyramid geometry. The trigonality indices **τ** values of the Na2 and the Na7 are respectively 0.1825 and 0.1033, respectively. These values are indicative of a distorted square pyramid around Na2 and Na7 atom. The **τ** value of 0.488 for Na5 is indicative of a severe distorted square pyramid geometry around the metal cation. However, when the modified index suggested by Konno et al. 33, χ = (β + γ + δ − 2α)/180 (which takes into account the other angles β and α are the largest angles, γ and δ are the other angles around the metal centers without the donor atoms defining β) is used, the χ value of 0.594 suggests that the geometry around the Na5 atom is a distorted trigonal bipyramid. Both τ (0.488) value and χ (0.594) value are close proximity to 0.5 and don’t permit to attribute unambiguously the geometry around Na5. The environment around each of the five hexacoordinated atoms (Na1, Na3, Na4, Na6 and Na8) is best described as a distorted octahedral geometry. For example, for Na1 atom, the basal plane of the environment is occupied by O14, O15, O12w and O30. The *cissoid* angles are in the range [75.85(8)°-112.16(7)°] while the *transoid* angles are 146.39(8)° [O14—Na1—O12w] and 159.51(8)° [O15—Na1—O30]. These values are severely different to the values of 90° and 180° expected by perfect square pyramidal geometry. The apical positions are occupied by O13W and O14W with an angle of 172.04(9)°. The sum of the angles subtended by atoms in the basal plane (365.51°) deviates severely from the ideal values of 360° indicating a severe distortion of the geometry around Na1. The atoms Na1, Na2, Na3 and Na4 form a plane (rms 0.0734) with a maximum deviation of 0.0763 (6) Å for Na4. The atoms Na5, Na6, Na7 and Na8 form a plane (rms 0.0673) with a maximum deviation of 0.0694 (6) Å for Na7. These two mean planes form a dihedral angle of 2.386 (2)°. In the crystal the two OH groups act in μ2-mode and bridge one Y and one Na atoms (Y2—O1A—Na4, Y4—O1B—Na5). The Y—OH bond lengths [Y2—O1A = 2.377 (2) Å, Y4—O1B = 2.396 (2) Å] are shorter than the Na—OH bond lengths [Na4—O1A = 2.637 (2) Å, Na4—O1B = 2.544 (2) Å]. One nitrate group acts in bidentate chelating mode with respect to Y1 and in monodentate mode with respect to Y2, bridging these two metal ions. The second nitrate group acts in the same fashion, bridging the Y3 and Y4 atoms. The distances Y—ONO2 [2.297(2) Å – 2.356(2) Å] are in the range reported for yttrium complexes 34,35. The distances Y—OLigand which are in the range [2.2873 (19) Å – 2.3528 (19) Å] are shorter than the distances reported for the complex (4-apyH)3[Y(pydc)3].4H2O (pydc = pyridine-2,6-dicarboxylate, 4-apy = 4-aminopyridine) 36 and the complex tetraaquahexakis(μ2-quinoline-4-carboxylato)diyttrium(III)dihydrate 37. The distances Y—N are in the range [2.505 (2) Å – 2.763 (3) Å] and agree with the distances reported for amino complex Y(HP-DO3A) (DO3A = 1,4,7,10-tetraazacyclododecane 1,4,7- triacetic acid) 38. The distances Na—Owater which are in the range [2.301 (2) Å – 2.543 (3) Å] are in the order of similar complexes 39,40. Numerous intra and inter molecular hydrogen bonds (Figure 5) consolidate the structure in a three-dimensional network (Figure 6).

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**Figure 5: Plot showing the inter and intramolecular hydrogens bonds in the crystal.**

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**Figure 6. The packing of the complex 1 in the crystal structure.**

# Conclusion

The reaction between yttrium nitrate and ethylenediaminetetraacetic acid disodium salt, in the presence of sodium hydroxide as a base, gave rise to a dodecanuclear complex containing four yttrium Y3+ ions and eight Na+ ions. The complex is characterized by spectroscopic and physicochemical methods. The structure is elucidated by XRD. Two of the four ligand molecules present in the complex act in η2, η1, η1, η2, η1, η1, η1, η1: μ5 mode, while the other two act in η2, η1, η2, η2, η1, η1, η1, η1: μ5 mode. Each yttrium ion is octacoordinated and is located in a N2O6 environment which is best described as a distorted square anti-prism. Three sodium ions are in an O5 environment described as a distorted square pyramid and five sodium ions are in an O6 environment described as a distorted octahedral geometry. The structure of the complex is consolidated by numerous intra and intermolecular hydrogen bonds.

**Supporting information**

CCDC-2435215contains the supplementary crystallographic data for the compounds (1) and (2) respectively. These data can be obtained free of charge via <https://www.ccdc.cam.ac.uk/structures/>, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK;

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