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Co-crystal structure of a dinuclear (Zn-Y) and a trinuclear (Zn-Y-Zn) complexes derived from a Schiff base ligand

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ABSTRACT

The present investigation describes the synthesis and structural study of a metal-zinc ligand [ZnL.H_2O], which was used to generate three dimensional supramolecular complex formulated as $[Y\{Zn(L)(SCN)\}(SCN)_2].[Y\{Zn(L)(SCN)\}_2(DMF)_2].(NO_3)$. The title compound crystallizes in the triclinic space group P-1 with the following unit cell parameters: a = 14.8987(7) Å, b = 15.6725(8) Å, c = 19.2339(10) Å, α = 94.610(4)°, β = 103.857(4)°, γ = 101.473(4)°, V = 4234.4(4) Å^3, Z = 2, R_1 = 0.063 and wR_2 = 0.96. For this compound, the structure reveals that one heterodinuclear unit $[Y\{Zn(L)(SCN)\}(SCN)_2]$ is co-crystallized with a heterotrinuclear unit $[Y\{Zn(L)(SCN)\}_2(DMF)_2].(NO_3)$. In the dinuclear moiety, the organic molecule acts as a hexadentate ligand and in the trinuclear unit, it acts as a pentadentate ligand with one of the oxygen methoxy group remaining uncoordinated. In both units the coordination environment of the zinc metal can be described as distorted square pyramidal. In the dinuclear unit the Y(III) is hexacoordinated while it is octacoordinated in the trinuclear unit. The environment of the Y(III) can be described as a distorted octahedral geometry in the dinuclear and as a distorted square antiprism in the trinuclear units respectively.

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1. Introduction

For over twenty years, the design and synthesis of heteropolynuclear complexes of d and f-block elements has taken very important steps [1-6]. This very dynamic field of research has made it possible to generate original structures with interesting properties in various fields such as magnetism [7,8], optics [9,10], catalysis [11,12] and luminescence [13,14]. The majority of compounds of this nature are compounds with 3d metals and rare earths 4f. Some compounds 4d-4f and 3d-5f are reported in the literature [15-19]. The 3d-4f compounds that are the most studied are of great interest to understand the nature of the exchanges between the ions from d and f elements combined in a molecular edifice [20-22]. Some of them showed original magnetic behavior. Organic ligands capable of maintaining the transition metal and the lanthanide ion by bridging the two ions are particularly desired. Organic molecules with phenolic oxygen atoms are often used to establish M-(di-μ-phenoxo)$_2$-Ln bridges in order to improve exchanges between metal centers [1,2]. It is in this perspective that the work we report focused on the use of the H_2L Schiff base (H_2L = *N*,*N*'-Phenylene-*bis*-(3-methoxysalicylideneimine)) which has two inners [23] capable to encapsulate two ions of different nature. In this work, we report the synthesis and structure of a heteropolynuclear co-crystal of zinc (II) and yttrium (III).

2. Experimental

2.1. Materials and physical methods

All the reagents and solvents were purchased from Aldrich and used without further purifications. Elemental (C, H and N) analyses were carried out using a LECO CHNS-932 instrument. IR spectra were recorded in the region 400–4000 cm^{-1} on a FTIR Perkin-Elmer Spectrum Two Spectrophotometer.

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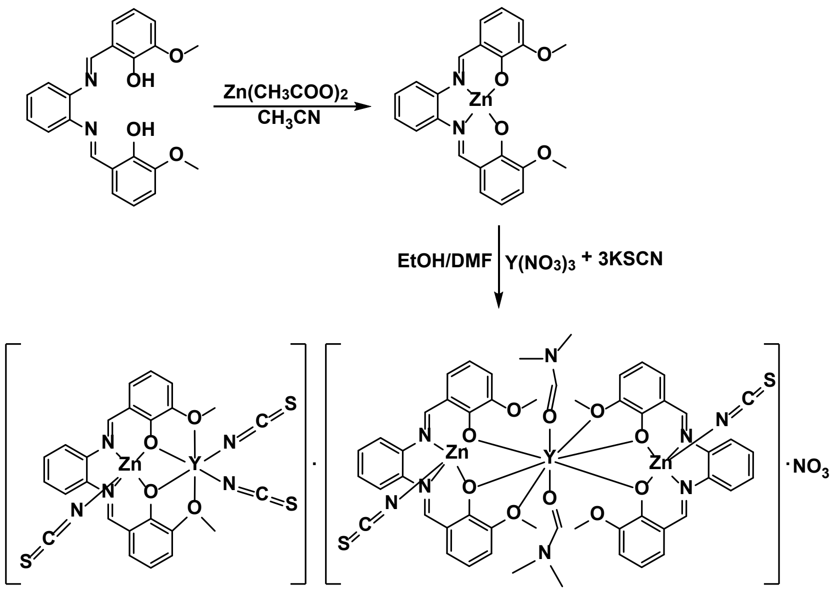


Scheme 1. Synthesis procedure of the ligand and the related complex.

Melting point was recorder on a Büchi apparatus and are uncorrected. The molar conductance of 10^{-3} M solutions of the metal complexes in DMF was measured at 25 °C using a WTW LF-330 conductivity meter with a WTW conductivity cell.

2.2. Synthesis

2.2.1. Synthesis of [(ZnL).(H_2O)]

The complex [(ZnL).(H_2O)] was prepared according to the experimental process described in the literature with slight modification [24]. To a solution of 1,2-diaminobenzene (0.250 g, 2.31 mmol) in 10 mL of acetonitrile was added a solution of *o*-vanillin (0.705 g, 4.62 mmol) in 10 mL of acetonitrile. The resulting orange mixture was refluxed for 60 min affording the organic H_2L ligand. After cooling, a solution of $Zn(CH_3COO)_2$. $2H_2O$ (0.507 g, 2.31 mmol) in 10 mL of acetonitrile was added. The mixture was heated under reflux for 60 min. On cooling the orange precipitate which appears was filtered off, washed with 3×10 mL of ether and dried in air yielding a compound formulated as [(ZnL).(H_2O)].

{6, 6'-Di-methoxy-2, 2'-[1, 2-phenylenebis(nitrilomethylidyne)]diphenolato-κ^{4}O, N, N'O'}zinc(II) monohydrate: Color: Orange. Yield: 75%. M.p.: 298-300 °C. FT-IR (KBr, ν, cm^{-1}): 3307 (OH) (br, water), 1609 (C=N) 1594 (C=C), 1586 (C=C), 1488 (C=C), 1439, 1234, 1187, 731. Anal. calcd. for $C_{22}H_{20}ZnN_2O_5$: C, 57.72; H, 4.40; N, 6.12. Found: C, 57.68; H, 4.42; N, 6.07 %. Λ (S cm^2 mol^{-1}): 5.

2.2.2. Synthesis of the co-crystal complex

The filtrate of a mixture of $Y(NO_3)_3.6H_2O$ (0.1915 g, 0.5 mmol) and KSCN (0.1458 g, 1.5 mmol) in 20 mL of absolute ethanol was added to a DMF solution (5 mL) of the [(ZnL).(H_2O)] (0.2288 g, 0.5 mmol). The resulting solution was heated under reflux for 2 hours. After cooling the solution was filtered and the filtrate was kept at 298 K. After four weeks crystals suitable for X-ray diffraction were collected and formulated as [Y{Zn(L)(SCN)}(SCN)$_2$].[Y{Zn(L)(SCN)}$_2$(DMF)$_2$].(NO_3)(Scheme 1).

Co-crystal (thiocyanato-2κ*O*){6, 6'-di-methoxy-2,2'-[1,2-phenylene-*bis*(nitrilomethylidyne)]diphenolato-κ^{8}1:2*O*^{6}, *O*^{1},*O*$^{1'}$, *O*$^{6'}$:-*O*^{1}, *N*, *N*', *O*$^{1'}$}*bis*(thiocyanato-1κN)zinc(II)yttrium(III) and *bis*{[(thiocyanato-2κO){6, 6'-di-methoxy-2, 2'-[1,2-phenylene-*bis*(nitrilomethylidyne)]diphenolato-*κ*^{4}*O*^{1}, *N*, *N*', *O*$^{1'}$}zinc(II)]*κ*^{3} *O*^{1}, *O*$^{1'}$, *O*^{6}}-*bis*(dimethylformamide-*κ*O)yttrium(III) nitrate: Color: Colorless. Yield: 60%. M.p.: 358-360 °C. FT-IR (KBr, ν, cm^{-1}): 2078 (S=C=N), 1648, 1609 (C=N), 1584 (C=C), 1545 (C=C), 1463 (C=C), 1440, 1384, 1287, 1237, 1189, 731, 673. Anal. calcd. for $C_{77}H_{68}Zn_3Y_2N_{14}O_{17}S_5$: C, 46.34; H, 3.43; N, 9.83; S, 8.03. Found: C, 46.36; H, 3.46; N, 9.79; S, 7.99 %. Λ_m (S.m^2.mol^{-1}): 173.

2.3. Crystal structure determination

Crystals suitable for X-diffraction, of the reported co-crystals, were grown by slow evaporation of DMF solution of the complex. Details of the X-rays crystal structure solution and refinement are given in Table 1. Diffraction data were collected using an ENRAF NONIUS Kappa CCD diffractometer with graphite monochromatized MoK_α radiation (λ = 0.71073 Å).Unit cell determination, data collection and integration were performed with APEX II and SAINT software [25]. All data were corrected for Lorentz and polarization effects. No absorption correction was applied. The structure was solved by direct methods which revealed the position of all non-hydrogen atoms and refined on F^2 by a full-matrix least-squares procedure using anisotropic displacement parameters for all non-hydrogen atoms [26,27]. The hydrogen atoms of water molecules and NH groups were located in the Fourier difference maps and refined. Others H atoms (=CH and CH_3 groups) were geometrically optimized and refined as riding model by AFIX instructions with U_{iso}(H) = 1.2 U_{eq}(C). Molecular graphics were generated using ORTEP-3 [28].

3. Results and discussion

3.1. General studies

Reaction of zinc(II) acetate and H_2L produces the mono-hydrated mononuclear zinc(II) complex [(ZnL).(H_2O)] (Scheme 1). The IR spectrum of compound [(ZnL).(H_2O)] exhibits a broad band at 3307 cm^{-1} due to the O–H stretching vibration of the lattice water molecule.

Table 1. Crystal data and structure refinement for [Y{Zn(L)(SCN)}(SCN)$_2$].[Y{Zn(L)(SCN)}$_2$(DMF)$_2$].(NO$_3$).

Formula	$C_{52}H_{50}N_8O_{10}S_2YZn_2{\cdot}C_{25}H_{18}N_5O_4S_3YZn{\cdot}NO_3$
FW	1995.68
Crystal shape/color	Prismatic/colorless
Crystal size (mm)	0.09 × 0.08 × 0.06
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	14.8987 (7)
b (Å)	15.6725 (8)
c (Å)	19.2339 (10)
α (°)	94.610 (4)
β (°)	103.857 (4)
γ (°)	101.473 (4)
V (Å^3)	4234.4 (4)
Z	2
D_{calc} (g.cm^{-3})	1.565
λ (MoKα) (Å)	0.71073
T (K)	293
μ (mm^{-1})	2.39
Index ranges	$-19 \le h \le 23$; $-24 \le k \le 21$; $-24 \le l \le 30$
$F(000)$	2024
θ range (°)	2.64-34.47
No. of measured reflections	39827
No. of independent reflections	30511
No. of observed [$I > 2\sigma(I)$] reflections	11814
R_{int}	0.040
$R[F^2 > 2\sigma(F^2)]$	0.063
$wR(F^2)$	0.96
Goodness-of-fit (Gof) on F^2	0.213
No. of parameters	1073
No. of restraints	0
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.85, −1.29

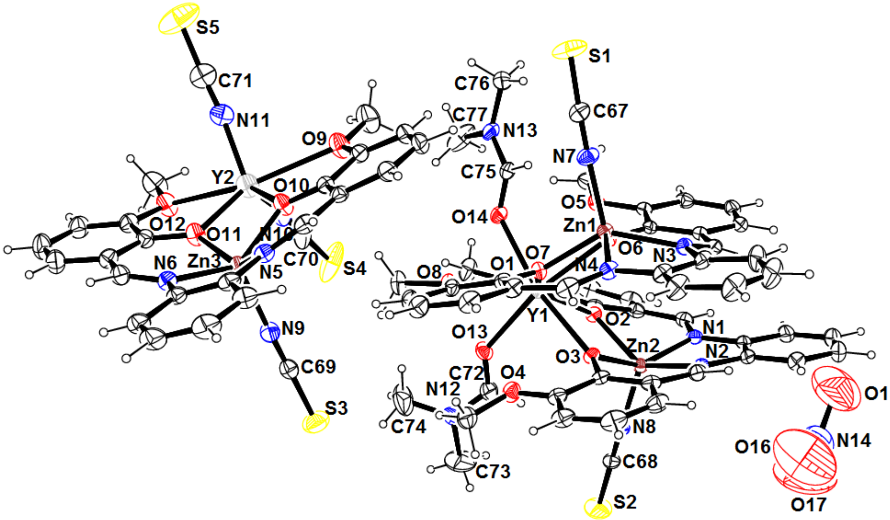


Figure 1. Crystal structure of the co-crystal complex. The labelling scheme of C atoms in the ligand are not shown for clarity. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small sphere.

The medium intensity band at 1609 cm^{-1} is indicative of the presence of a C=N function which is coordinated through the azomethine atom. The bands pointed in the region 1594-1488 cm^{-1} are attributed to the aromatic ring.

On treated with a mixture of Y(NO$_3$)$_3$.6H$_2$O and KSCN in DMF/ethanol, the pentanuclear compound [Y{Zn(L)(SCN)}(SCN)$_2$].[Y{Zn(L)(SCN)}$_2$(DMF)$_2$].(NO$_3$) was obtained on standing for four weeks as colorless crystals (Scheme 1). The IR spectrum of this compound exhibits a sharp medium intensity band at 2078 cm^{-1} which is characteristic of a coordinated thiocyanate group [29]. Additional bands at 1648 and 1609 cm^{-1} are observed and are attributed, respectively, to the coordinated molecule solvent of DMF and the coordinated C=N group. The bands due to the aromatic ring are pointed in the region 1584-1440 cm^{-1}. A sharp and intense band at 1383 cm^{-1} is indicative of the presence of a non-coordinated nitrate group. The molar conductivity which is 5 S.cm^2.mol^{-1} for [(ZnL).(H$_2$O)] shows that the complex is a neutral electrolyte in DMF solution. For the [Y{Zn(L)(SCN)}(SCN)$_2$].[Y{Zn(L)(SCN)}$_2$(DMF)$_2$].(NO$_3$), the molar conductivity of 173 S.cm^2.mol^{-1} is indicative of a 1:1 electrolyte in DMF solution [30].

3.2. Structure description of complex 1 and 2

The asymmetric unit of the structure (Figure 1) of [Y{Zn(L)(SCN)}(SCN)$_2$].[Y{Zn(L)(SCN)}$_2$(DMF)$_2$].(NO$_3$) contains two different entities. One neutral dinuclear moiety [Y{Zn(L)(SCN)}(SCN)$_2$] which co-crystallize with a mono charged trinuclear unit [Y{Zn(L)(SCN)}$_2$(DMF)$_2$]$^+$. The dinuclear and trinuclear units are shown in Figure 1, while selected bond lengths and angles of the coordination environment of the metal centers are listed in Table 2. In the dinuclear unit, the Zn3 atom and the Y2 atom are bridged by two phenoxo oxygen atoms.

Table 2. Selected bond lengths (Å) and bond angles (°) for the co-crystal.

Atom-Atom	Bond lengths (Å)	Atom-Atom	Bond lengths (Å)
Y1-O7	2.256 (3)	Zn1-N7	1.972 (4)
Y1-O13	2.265 (3)	Zn1-O7	2.001 (3)
Y1-O2	2.279 (3)	Zn1-O6	2.044 (3)
Y1-O14	2.305 (3)	Zn1-N3	2.051 (4)
Y1-O3	2.332 (3)	Zn1-N4	2.078 (4)
Y1-O6	2.360 (3)	Zn2-N8	1.969(4)
Y1-O8	2.672 (3)	Zn2-O2	2.014 (3)
Y1-O1	2.717 (3)	Zn2-O3	2.022 (3)
Y1-Zn1	3.4568 (7)	Zn2-N2	2.054 (4)
Y1-Zn2	3.4627 (7)	Zn2-N1	2.059 (4)
Y2-N10	1.923 (6)	Zn3-N9	1.972 (5)
Y2-N11	1.944 (6)	Zn3-O10	2.004 (3)
Y2-O11	2.020 (3)	Zn3-O11	2.006 (3)
Y2-O10	2.029 (3)	Zn3-N5	2.049 (4)
Y2-O12	2.613 (4)	Zn3-N6	2.051 (4)
Y2-O9	2.622 (4)	N7-C67	1.141 (6)
S1-C67	1.608 (6)	N8-C68	1.124 (6)
S2-C68	1.610 (5)	N9-C69	1.119 (6)
S3-C69	1.606 (6)	N10-C70	1.156 (8)
S4-C70	1.603 (9)	N11-C71	1.118 (8)
S5-C71	1.605 (8)		
Atom-Atom-Atom	**Bond angles (°)**	**Atom-Atom-Atom**	**Bond angles (°)**
O7-Y1-O13	118.38 (12)	N7-Zn1-O6	104.04 (15)
O7-Y1-O2	137.11 (11)	N7-Zn1-N3	112.81 (17)
O7-Y1-O14	90.12 (11)	O7-Zn1-N3	138.24 (14)
O13-Y1-O14	105.98 (12)	O6-Zn1-N3	90.02 (14)
O2-Y1-O14	113.81 (11)	N7-Zn1-N4	108.99 (17)
O7-Y1-O3	80.62 (11)	O6-Zn1-N4	146.88 (13)
O13-Y1-O3	88.17 (12)	O6-Zn1-N3	90.02 (14)
O2-Y1-O3	67.89 (10)	N8-Zn2-O2	104.30 (15)
O14-Y1-O3	165.61 (12)	N8-Zn2-O3	106.59 (14)
O13-Y1-O6	167.56 (11)	N8-Zn2-N2	119.04 (16)
O2-Y1-O6	79.09 (10)	O2-Zn2-N2	136.59 (13)
O14-Y1-O6	83.86 (11)	N8-Zn2-N1	104.10 (16)
O2-Y1-O8	159.38 (11)	O3-Zn2-N1	148.73 (14)
O3-Y1-O8	114.01 (10)	Zn2-O2-Y1	107.36 (12)
O6-Y1-O8	121.40 (10)	Zn2-O3-Y1	105.12 (12)
O7-Y1-O1	158.33 (11)	Zn1-O7-Y1	108.43 (12)
O3-Y1-O1	121.05 (11)	Zn1-O6-Y1	103.19 (11)
O6-Y1-O1	111.55 (10)	N7-C67-S1	178.1 (6)
O8-Y1-O1	105.91 (10)	N8-C68-S2	177.8 (5)
N10-Y2-N11	120.4 (2)	N9-Zn3-O11	108.50 (18)
N10-Y2-O11	114.5 (2)	O10-Zn3-O11	78.02 (14)
N11-Y2-O11	111.36 (19)	N9-Zn3-N5	108.16 (18)
N10-Y2-O10	113.1 (2)	O10-Zn3-N5	88.24 (16)
N11-Y2-O10	112.44 (19)	O11-Zn3-N5	143.31 (16)
O10-Y2-O12	142.38 (13)	N9-Zn3-N6	110.67 (17)
Zn3-O10-Y2	100.98 (16)	O10-Zn3-N6	139.42 (16)
Zn3-O11-Y2	101.22 (16)	N11-C71-S5	177.1 (8)
N9-C69-S3	179.0 (5)	N10-C70-S4	178.3 (8)

In both units, the Zn center is coordinated to two phenoxo oxygen atoms, two imino nitrogen atoms from the azomethine group of the ligand and one nitrogen atom from the thiocyanate group resulting thereby to a pentacoordinated Zn center. The stereochemistry of the Zn(II) ions in both dinuclear and trinuclear units are best described as distorted square pyramidal. In fact, the *Addison* parameter [31] $\tau = (\beta-\alpha)/60$ where α and β are the largest values of the bond angles around Zn(II) ion can be used to attributed the geometry of a penta-coordinated metal complex. When the geometry is a perfect square-pyramidal $\tau = 0$ and when $\tau = 1$ a perfect trigonal bipyramidal geometry is obtained. In the penta-coordinated environment of Zn3, Zn1 and Zn2 the values of τ are, respectively, 0.065, 0.144 and 0.202 indicating that the geometry around both Zn(II) ions can be described as distorted square pyramidal (Figure 2a). The extent of the distortion is greater for Zn1 and Zn2 which are in the trinuclear unit. In the case of Zn3 in the dinuclear unit, the basal plane is defined by N5, N6, O11 and O10 and the apical position is occupied by N9 from the thiocyanate ligand. For the metal centers Zn1 and Zn2 in the trinuclear unit the basal planes are respectively defined by N3, N4, O7, O6 and O2, O3, N2, N1 while the nitrogen atoms N7 and N8 from the thiocyanate groups occupied respectively the axial positions.

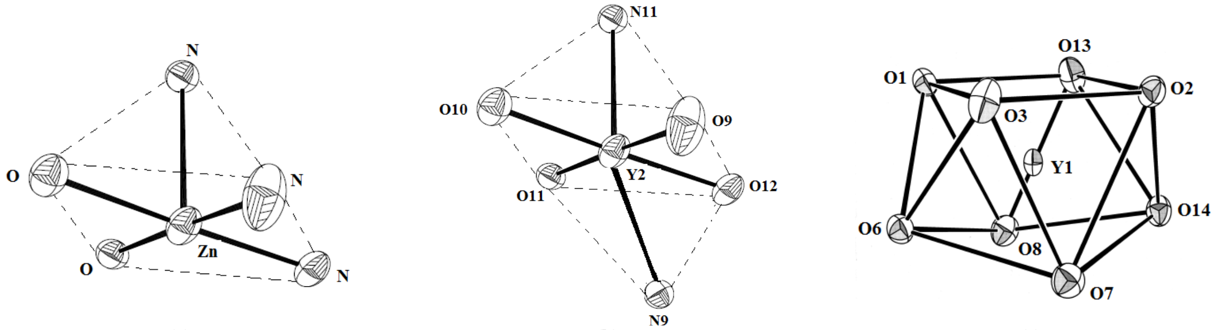
In the dinuclear unit the Y(III) ion is hexacoordinated by two phenoxo oxygen atoms and two methoxy oxygen atoms from the ligand. Two nitrogen atoms from thiocyanate groups complete the coordination sphere. The environment around the Y2 atom can be described as a distorted square bipyramid, the basal plane being occupied by two bridged phenoxo oxygen atoms (O10 and O11) and two methoxy oxygen atoms O12 and O9. The two axial position are occupied by two nitrogen atoms of thiocyanate groups N10 and N11 (Figure 2b).

In the basal planes of the square pyramidal geometries, the Zn-O distances are the shortest bond lengths and fall into the range 2.044(3) - 2.001(3) Å for both dinuclear and trinuclear units while the $Zn\text{-}N_{imino}$ distances are the longest bond lengths and are in the range 2.078(4) - 2.049(3) Å. Those values are close proximity with those found for the complex $[Zn(L)(\mu_{1,1}\text{-}NCS)\text{-}Zn(L)(NCS)(H_2O)]$ [32] where HL is 2-((2-(dimethyl amino)ethylimino)methyl)-6-methoxyphenol. The Zn-N distances involving the anionic thiocyanate in axial position which are the shortest bond lengths (Zn1-N7 = 1.972(4) Å, Zn2-N8 = 1.969(4) Å and Zn3-N9 = 1.972(5) Å) are comparable to the bond lengths found for the complex $[Zn_3L_2(NCS)_2]$ [33], where H_2L is 2-(3-(2-(2-hydroxy-3-methoxybenzylideneamino)ethyl)oxazolidin-2-yl)-6-methoxy phenol.

Table 3. Hydrogen-bond geometry (Å, °).

D*-H···*A	***D*-H (Å)**	**H···*A* (Å)**	***D*···*A* (Å°)**	***D*-H···*A* (°)**
C1-H1AB···S2 ^{i}	0.96	2.79	3.716(6)	162.4
C23-H23A···S4 ^{ii}	0.96	3.01	3.602(6)	121.4
C45-H45C···N13	0.96	2.58	3.440(9)	149.7
C77-H77B···S4 ^{ii}	0.96	2.99	3.753(7)	137.6

Symmetry codes: (i) −*x*, −*y*+1, −*z*+2; (ii) −*x*+1, −*y*+1, −*z*+2.



(a) (b) (c)

Figure 2. Plot showing the coordination sphere in the co-crystal of (**a**) Zn(II) in both dinuclear and trinuclear unit, (**b**) Y(III) in the dinuclear unit and (**c**) Y(III) in the trinuclear unit.

In the trinuclear moiety the Y1 atom is diphenoxo-bridged to Zn1 and Zn2 atoms, respectively. The yttrium(III) ion is octacoordinated by four phenoxo oxygen atoms which acts as bridged with Zn1 (O6 and O7) and Zn2 (O2 and O3) respectively and two oxygen atoms from dimethylformamide molecules solvent. The resulting coordination polyhedron is best described as a distorted square antiprism where the two square faces are respectively defined by [O1, O3, O2, O13] and [O7, O6, O8, O14] (Figure 2c).

In the dinuclear unit all the methoxy oxygen atoms are coordinated to the yttrium ion whereas in the trinuclear unit for each of the two metal-ligands one of the methoxy atoms remains uncoordinated (O4 and O5).

In both dinuclear and trinuclear units of the co-crystal, the Y-O$_{\text{phenoxo}}$ bonds have the shortest distances which fall in the range 2.020(3) - 2.360(3) Å. These values are comparable with the distances for a trinuclear complex $[\{LNiY(H_2O)_4\}\{W(CN)_8\}]_\infty$.9.5$H_2O$ obtained from an analogous ligand [34]. The Y-O$_{\text{methoxy}}$ are the longest distances in the two different units 2.613(4) - 2.717(3) Å and are longer than those reported for the above compound in which the value of the mean distances of the Y-O$_{\text{methoxy}}$ is 2.557 Å [30]. In the trinuclear unit, the two Y-O$_{\text{DMF}}$ distances are worth 2.265(3) and 2.305(3) Å.

In both units the Zn(di-μ-phenoxo)Y bridging fragments show a difference between the Zn-O and Y-O binding lengths whose mean values are 2.005 and 2.308 Å, respectively, for the dinuclear complex and 2.020 and 2.307 Å for the trinuclear complex. The angles Zn-O-Y have different values with average values of 101.10° in the dinuclear unit and 104.98° in the trinuclear unit. These observations are indicative of an asymmetry in the Zn(di-μ-phenoxo)Y bridging fragments.

In the dinuclear unit the dihedral angle between Zn3-O10-O11 and Y2-O10-O11 planes is equal to 15.67(20)°. In the trinuclear unit the dihedral angles between the planes Zn1-O6-O7 and Y1-O6-O7 and the planes Zn2-O2-O3 and Y1-O2-O3 are equal to 6.53(9)° and 5.38(18)°, respectively. These observations show that the structure is more twisted in the dinuclear unit than in the trinuclear unit. The Zn–Y distances are quite short: 3.4568(7) and 3.4627(7) Å in the trinuclear unit and 3.1110(8) Å in the dinuclear unit.

The deformation of the coordination polyhedron around each zinc atom is confirmed by the values of the angles around the zinc atom. In fact, the values of the *transoid* angles (138.24(14)° and 146.88(13)° for Zn1; 136.59(13)° and 148.73(14)° for Zn2; 139.42(16)° and 143.31(16)° for Zn3) and the *cisoid* angles [79.64(11)° and 79.55(16)° for Zn1; 79.29(11)° and 80.08(17)° for Zn2; 78.02(14)° and 80.02(17)° for Zn3] in the basal plane of each zinc atom are different from the ideal angles for a square planar octahedron. For both Zn center, the angles between the N atom in apical position and each of the four atoms in the basal plane are largely greater than the ideal value of 90° and fall in the range 104.04(15) - 119.04(16)°. The octahedral geometry around Y2 is also strongly distorted as shown by the value of the angle between the atoms in apical position N10-Y2-N11 = 120.4(2)° and the angles sum in the basal plan which being 359.73°. The Zn1-Y1-Zn2 angle value of 91.125 (16) is indicative of not aligned three metal centers. The whole anionic N-donor thiocyanates are quasi-linear with angle N-C-S in the range 177.1(8) - 179.0(5)°. These anionic N-donor thiocyanate bind almost linearly to the zinc (II)/yttrium (III) ions in both dinuclear and trinuclear units with angle M-N-CS (M = Zn or Y) in the range 171.4(6) -178.0(5)°. The best linearity is found in the trinuclear unit (Zn-N-CS = 178.0(5)°) while the least linearity is found in the dinuclear unit (Y-N-CS = 171.4(6)°).

The four atoms of the bridging entities ZnO_2Y are not ideally coplanar. The deviations from the mean planes are 0.0535(11) Å for Zn1,-0.0462(10)Å for O6, -0.0507(11) Å for O7, 0.0435(9) Å for Y1 (Plane Zn1-O6-O7-Y1); 0.0442(11) Å for Zn2, -0.0408(11) Å for O2, -0.0393(10) Å for O3, 0.0359(9) Å for Y1 (Plane Zn2-O2-O3-Y1) and 0.1079(14) Å for Zn3, -0.1068(14) Å for O10, -0.1072(14) Å for O11, 0.1061(14) Å for Y2 (Plane Zn3-O10-O11-Y2).

The dinuclear and trinuclear units of the asymmetric unit are connected by hydrogen bonds of type C$_{\text{methoxy}}$-H…N$_{\text{DMF}}$ (C45-H…N13) (Figure 3, Table 3). While, weak intermolecular hydrogen bonds involving C$_{\text{methoxy}}$ (or C$_{\text{DMF}}$) as C atom donor and S-acceptor thiocyanate link dinuclear and trinuclear units belonging to different asymmetric units. The combined hydrogen bonds links give rise to a three-dimensional network architecture. It should be noted that the nitrate ion is by no means engaged in any interaction in the structure, playing thereby the only role of counter ion.

4. Conclusion

The reported work is concerned with the synthesis and the structural study of a dinuclear-trinuclear co-crystal derived

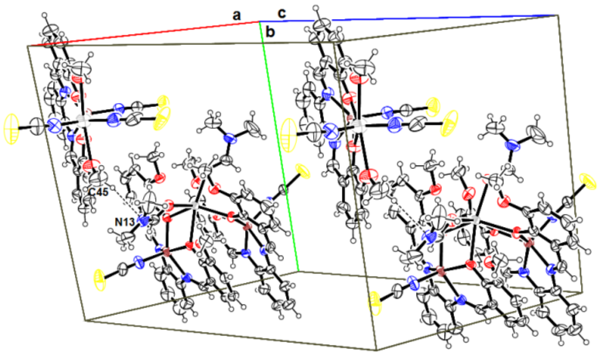


Figure 3. Perspective view of the three dimensional supramolecular network constructed by hydrogen bond interactions.

from the organic molecular ligand, *N,N'*-1,2-phenylene-*bis*-(3-methoxysalicylaldimine). In the yielded co-crystal, there are two different environments for the yttrium atom. In the dinuclear unit the Y(III) is hexacoordinated while it is octacoordinated, while in the trinuclear unit, with a distorted square antiprism environment. In both units, three ions of Zn(II) present in the complex are pentacoordinated in the same fashion. In dinuclear unit, all the methoxy oxygen atoms are coordinated while the trinuclear unit shows that only one methoxy oxygen atom to each ligand is coordinated and the second methoxy oxygen atom remains uncoordinated. The dinuclear unit interact with the trinuclear unit through C-H…N hydrogen bonds in the asymmetric unit and through C-H…S belonging two different asymmetric units.

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Supporting information

CCDC-1824581 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via https://www.ccdc.cam.ac.uk/structures/, or by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033.

Disclosure statement

Conflict of interests: The authors declare that they have no conflict of interest.
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