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Syntheses, Crystal Structures and Thermal Behaviors of Two Supramolecular Salamo-Type Cobalt(II) and Zinc(II) Complexes

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Abstract: This paper reports the syntheses of two new complexes, $[Co(L^1)(H_2O)_2]$ (1) and $[{Zn(L^2) (\mu-OAc)Zn(n-PrOH)}_2]$ (2), from asymmetric halogen-substituted Salamo-type ligands H_2L^1 and H_3L^2 , respectively. Investigation of the crystal structure of complex 1 reveals that the complex includes one Co(II) ion, one $(L^1)^{2-}$ unit and two coordinated water molecules. Complex 1 shows slightly distorted octahedral coordination geometry, forming an infinite 2D supramolecular structure by intermolecular hydrogen bond and π - π stacking interactions. Complex 2 contains four Zn(II)ions, two completely deprotonated $(L^2)^{3-}$ moieties, two coordinated μ -OAc⁻ ions and n-propanol molecules. The Zn(II) ions in complex 2 display slightly distorted trigonal bipyramidal or square pyramidal geometries.

Keywords: salamo-type ligand; complex; synthesis; crystal structure; supramolecular interaction

1. Introduction

Recently, increasing attention has also been absorbed in coordination chemistry of Salen-type N₂O₂ chelating metal complexes owing to their various kinds of functionalities [1–8]. A part of the metal complexes are used as host–guest chemistry [9–17], magnetism [18–25], electrochemistry [26,27], biological activities [28–34], optical properties [35–43], catalysis [44,45], molecular recognition [35,36,46,47], and so forth. It is clear that the architectures of coordination molecule comprise metal ions (and metal clusters) that serve the roles of nodes and organic ligands as bridges. These exhibits diverse infinite one-dimensional (1D), two-dimensional (2D) models with various exciting structural features, resulting coordination bonding, hydrogen bonding, aromatic π – π stacking interactions as well as van der Waals forces [48].

Salen-type N₂O₂compounds are capable of forming different types of complexes due to their several electron-rich donor centers [49] and the tautomerism effect of the enol and keto forms [50]. Meanwhile, on account of the fact that the high electronegative oxygen atoms affect azomethine nitrogen and N₂O₂ coordination plane on the basis of Salamo-type bisoxime ligands [45,51–55], many complexes exhibit abundant interests, attractive structures and properties have been well documented [56–59]. Furthermore, metal ions play key roles in wide range of differing biological processes and the interaction of the metal ion with drugs employed for therapeutic reasons is a subject of considerable interest [60]. Herein, following our previous studies on the syntheses, structural characterizations and optical properties of Salamo-type complexes with the d⁵ and d¹⁰ group elements [49,61], we report the syntheses and structural characterizations of mononuclear Co(II) and tetranuclear Zn(II) complexes, $[Co(L^1)(H_2O)_2]$ (1), $[{Zn(L^2)(\mu-OAc)Zn(n-PrOH)}_2]$ (2) based on Salamo-type N₂O₂/N₂O₃ligands (H₂L¹

= 4,6-dibromo-4',6'-dichloro-2,2'-[ethylenediyldioxybis(nitrilomethylidyne)]diphenol; H_3L^2 = 6-hydroxy-4'-chloro-2,2'-[ethylenediyldioxybis(nitrilomethylidyne)]diphenol), and the molar conductance, IR, UV-Vis spectra, TG-DTG and X-ray crystal structures were also investigated.

2. Experimental

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication, No. CCDC 1511309 and 1511310 for complexes **1** and **2**. Copies of these data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (Telephone: (44) 01223 762910; Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk). These data can also be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html.

2.1. Materials and Methods

3,5-Dichlorosalicylaldehyde, 3,5-dibromosalicylaldehyde, 5-chlorosalicylaldehyde and 3-hydroxysalicylaldehyde were purchased from a Acros Organics company (New York, NY, USA) and used without further purification. The other reagents and solvents were analytical grade acquired from Tanjin Chemical Reagent Factory (Tianjin, China).

C, H, and N analyses were obtained using a GmbH VarioEL V3.00 automatic elemental analysis instrument (Berlin, Germany). Elemental analyses for Co(II) and Zn(II) were detected by an IRIS ER/S·WP-1 ICP atomic emission spectrometer (Berlin, Germany). Molar conductance value measurements were carried out on a model DDS-11D type conductivity bridge (The United States CHI)using 1.0×10^{-3} mol·L⁻³ solution in DMF at 18 °C. IR spectra were recorded on a Vertex70 FT-IR spectrophotometer (Bruker AVANCE, Billerica, MA, USA), with samples prepared as KBr (400–4000 cm⁻¹) pellets. UV–Vis absorption spectra were recorded on a Shimadzu UV-2550 spectrophotometer (Shimadzu, Japan) in ethanolic solution. ¹H NMR spectra were determined by a German Bruker AVANCE DRX-400 spectrometer (Bruker AVANCE, Billerica, MA, USA). DSC-TG analyses were carried out at a heating rate of 10 °C/min on a NETZSCH STA 449 F3 thermoanalyzer (NETZSCH Group, Germany). X-ray single crystal structures were determined on a Bruker Smart APEX CCD area detector (Bruker AVANCE, Billerica, MA, USA). Melting points were measured by the use of a microscopic melting point apparatus made in Beijing Taike Instrument Limited Company, and the thermometer was uncorrected.

2.2. Synthesis of H_2L^1

The major reaction step, containing the synthesis of 4,6-dibromo-4',6'-dichloro-2,2'-[ethylenediyldioxybis(nitrilomethylidyne)]diphenol (H_2L^1) and 6-hydroxy-4'-chloro-2,2'-[ethylenediyldioxybis(nitrilomethylidyne)]diphenol (H_3L^2), is given in Scheme 1.



Scheme 1. Syntheses route to H_2L^1 and H_3L^2 .

1,2-Bis(aminooxy)ethane was prepared by an analogous method reported earlier [35,36]. Yield: 56.8%. Anal. Calcd for C₂H₈N₂O₂ (%): C, 26.08; H, 8.76; N, 30.42. Found: C, 25.97; H, 8.70; N, 30.49.

2-[*O*-(1-ethyloxyamide)]oxime-4,6-dichlorophenol: A solution of 3,5-dichlorosalicylaldehyde (382.02 mg, 2.0 mmol) in ethanol (40 mL) was added to a solution of 1,2-bis(aminooxy)ethane (368.4 mg, 4.0 mmol) in ethanol (100 mL), then the mixture was subjected to heating at 50–55 °C for 6 h. The solution was concentrated in vacuo and the residue was purified by column chromatography (SiO₂, chloroform/ethyl acetate, 25:1) to afford crystals of 2-[*O*-(1-ethyloxyamide)]oxime-4,6-dichlorophenol. Yield: 65.6%, m.p. 92–93 °C. Anal. Calcd for C₉H₁₀Cl₂N₂O₃ (%): C, 40.78; H, 3.80; N, 10.57. Found: C, 40.72; H, 3.69; N, 10.63.

4,6-Dibromo-4',6'-dichloro-2,2'-[ethylenediyldioxybis(nitrilomethylidyne)]diphenl (H₂L¹): A solution of the obtained 2-[*O*-(1-ethyloxyamide)]oxime-4,6-dichlorophenol (384.38 mg, 1.45 mmol) in ethanol (15 mL) was added to a solution of 3,5-dibromosalicylaldehyde (406.00 mg, 1.45 mmol) in ethanol (15 mL) and the mixture was subjected to heating at 50–55 °C for 8 h. After cooling to room temperature, the resulting white precipitates were collected. Yield: 79.8%, m.p. 184–185 °C. ¹H NMR (400 MHz, CDCl₃) δ 10.48 (s, 1H), 10.32 (s, 1H), 8.15 (d, *J* = 10.5 Hz, 2H), 7.65 (d, *J* = 2.2 Hz, 1H), 7.37 (d, *J* = 2.4 Hz, 1H), 7.25 (s, 1H), 7.08 (d, *J* = 2.4 Hz, 1H), 4.48 (d, *J* = 20.8 Hz, 4H). Anal. Calcd for C₁₆H₁₂Br₂Cl₂N₂O₄ (%): C, 36.47; H, 2.30; N, 5.32. Found: C, 36.40; H, 2.35; N, 5.29.

2.3. Synthesis of H_3L^2

2-[*O*-(1-ethyloxyamide)]oxime-4-chlorophenol: A solution of 5-chlorosalicylaldehyde (314.00 mg, 2.0 mmol) in ethanol (50 mL) was added to a solution of 1,2-bis(aminooxy)ethane (368.00 mg, 4.0 mmol) in ethanol (100 mL) and the mixture was subjected to heating at 50–55 °C for 6 h. The solution was concentrated in vacuo and the residue was purified by column chromatography (SiO₂, chloroform/ethyl acetate, 20:1) to afford crystals of 2-[*O*-(1-ethyloxyamide)]oxime-4-chlorophenol. Yield: 59.9%, m.p. 70–71 °C. Anal. Calcd for C₉H₁₁ClN₂O₃ (%): C, 46.87; H, 4.81; N, 15.37. Found: C, 46.80; H, 4.90; N, 15.32.

6-Hydroxy-4'-chloro-2,2'-[ethylenediyldioxybis(nitrilomethylidyne)]diphenol (H₃L²): A solution of the obtained 2-[*O*-(1-ethyloxyamide)]oxime-4-chlorophenol (385.77 mg, 1.67 mmol) in ethanol (15 mL) was added to a solution of 3-hydroxysalicylaldehyde (234.60 mg, 1.70 mmol) in ethanol (20 mL) and the mixture was subjected to heating at 50–55 °C for 6 h. After cooling to room temperature, white precipitates of the desired product were collected. Yield: 80.7%, m.p. 132–133 °C. ¹H NMR (400 MHz, CDCl₃) δ 4.43 (d, *J* = 19.6 Hz, 4H), 7.12 (s, 1H), 7.39 (d, *J* = 2.5 Hz, 2H), 7.48 (d, *J* = 2.4 Hz, 2H), 7.57 (s, 1H), 7.69 (d, *J* = 2.5, Hz, 2H), 8.02 (s, 1H), 8.34 (s, 1H). Anal. Calcd for C₁₆H₁₅ClN₂O₅ (%): C, 54.79; H, 4.31; N, 7.99. Found: C, 54.67; H, 4.36; N, 8.01.

2.4. Synthesis of Complex 1

A pink, transparent n-propanol solution (2 mL) of cobalt(II) acetate tetrahydrate (3.30 mg, 0.013 mmol) was added dropwise to a colorless mixed solution of CH_2Cl_2 and CH_3CN (4 mL) of H_2L^1 (3.85 mg, 0.007 mmol) at room temperature. The color of the mixed solution turned to yellow immediately, the filtrate was allowed to stand at room temperature for about two weeks, after which light-yellow prismatical single crystals suitable for X-ray structural determination were obtained by the slow evaporation from mixed solution. Anal. Calcd for $C_{16}H_{14}Br_2Cl_2CoN_2O_6$ (%): C, 31.00; H, 2.28; N, 4.52; Co, 9.51. Found: C, 29.88; H, 2.26; N, 4.60; Co, 9.48.

2.5. Synthesis of Complex 2

A colorless, transparent n-propanol solution (2 mL) of zinc(II) acetate tetrahydrate (4.51 mg, 0.021 mmol) was added dropwise to a colorless acetonitrile solution (4 mL) of H_3L^2 (3.49 mg, 0.010 mmol) at room temperature. The color of the mixing solution was immediately turned to yellow, and the filtrate was left to stand at room temperature for about two weeks, after which light-yellow prismatical single crystals suitable for X-ray structural determination were obtained by the slow evaporation from mixed solution. Anal. Calcd for $C_{42}H_{46}Cl_2N_4O_{16}Zn_4$ (%): C, 42.20; H, 3.88; N, 4.69; Zn, 21.88. Found: C, 42.16; H, 3.84; N, 4.70; Zn, 21.79.

2.6. Crystal Structure Determinations of Complexes 1 and 2

Single crystal X-ray diffraction data of complexes **1** and **2** were collected at 293(2) and 228(3) K, respectively, on a BRUKER SMART APEX II CCD diffractometer with graphite monochromated Mo-*K* α radiation ($\lambda = 0.71073$ Å). The LP factor semi-empirical absorption corrections were applied using the SADABS program. The structures were solved by direct methods using SHELXS and refinement was done against F^2 using SHELXL. The non-hydrogen atoms were refined anisotropically; hydrogen atoms were positioned geometrically (C–H = 0.93, 0.96 and 0.97 Å) and were refined as riding, with $U_{iso}(H) = 1.20$ or $1.50 U_{eq}(C)$. The crystal data and experimental parameters relevant to the structure determinations are listed in Table 1 and the final positional and thermal parameters are available as Supplementary Materials.

Complex	1	2
Formula	C ₁₆ H ₁₄ Br ₂ Cl ₂ CoN ₂ O ₆	C ₄₂ H ₄₆ Cl ₂ N ₄ O ₁₆ Zn ₄
Formula weight	619.94	1195.21
Temperature (K)	293(2)	228(1)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	<i>P</i> 2(1)/c	<i>P</i> -1
Unit cell dimensions		
a (Å)	24.8201(9)	9.067(1)
b (Å)	10.1475(4)	11.72(1)
<i>c</i> (Å)	7.8671(3)	12.437(1)
α (°)	90	91.649(9)
β (°)	91.459(3)	108.56(1)
γ (°)	90	104.51(1)
V (Å ³)	1980.8(1)	1204.4(2)
Z	4	1
$D_c ({\rm g}{\rm cm}^{-3})$	2.079	1.648
μ (mm ⁻¹)	5.209	2.151
F (000)	1212.0	608.0
Crystal size (mm)	0.21 imes 0.06 imes 0.04	0.24 imes 0.21 imes 0.19
θ Range (°)	3.36–26.02	3.43-26.02
	$-30 \le h \le 24$	$11 \leq h \leq 7$
Index ranges	$-12 \leq k \leq 10$	$-14 \leq k \leq 13$
	$-9 \le l \le 8$	$-15 \leq l \leq 14$
Reflections collected	8023	8045
Independent reflections	3891	4729
R _{int}	0.0412	0.0414
Completeness to $\theta = 26.32$	99.8%	99.6%
Data/restraints/parameters	3891/0/264	4729/4/312
GOF	1.038	1.044
Final R_1 , wR_2 indices $[I > 2\sigma(I)]$	0.0480/0.0763	0.0441/0.0988
$R_{\rm e}$ $wR_{\rm e}$ indices (all data)	0.0816 / 0.0800	0.0664/0.1167
	0.0010/0.0090	(a)111111
Largest differences	0.513/-0.559	0.412/-0.480
	peak and hole (e ${ m \AA}^{-3}$)	

Table 1. Crystal data and structure refinement parameters for complexes 1 and 2.

3. Results and Discussion

Complexes 1 and 2 with the Salamo-type bisoxime chelating N_2O_2/N_2O_3 ligands (H_2L^1 and H_3L^2) have been duly synthesized, and structurally characterized by molar conductance, IR spectra, UV-Vis spectra, DSC-TG and X-ray crystallography analyses.

3.1. Molar Conductance

Complexes 1 and 2 are both soluble in DMF and DMSO, but insoluble in CHCl₃, CH₂Cl₂, EtOH, MeOH, MeCN, THF, acetone, ethyl acetate and n-hexane. Only complex 1 displays good stability in air at room temperature while complex 2 shows relative instability. Moreover, the ligands (H₂L¹ and H₃L²) are both soluble in the above solvents. The molar conductance values of complexes 1 and 2 in 1.0×10^{-3} mol·L⁻³ DMF solutions are 2.2 and 2.9 Ω^{-1} ·cm²·mol⁻¹, respectively, with the implication that complexes 1 and 2 are non-electrolytes.

3.2. Crystal Structure of Complex 1

The results of the X-ray structural study reveal that complex 1 crystallizes in the monoclinic system and P2(1)/c space group. As depicted in Figure 1, complex 1 concludes one Co(II) ion together with one deprotonated ligand $(L^{1})^{2-}$ unit (in the form of enol), and two coordinated water molecules. The Co(II) ion is hexa-coordinated by two oxime nitrogen (N1 and N2) atoms and two deprotonated phenoxo oxygen (O1 and O4) atoms, the four atoms are all from one deprotonated $(L^{1})^{2-}$ unit, and two oxygen (O5 and O6) atoms from two coordinated water molecules. The coordination environment around the Co(II) ion is best described as a slightly distorted octahedral geometry (Figure 1). This shows a correlation to the reported trinuclear [Co₃(5-NO₂salamo)₂(OAc)₂(MeOH)₂]·2MeOH, in which the Co(II) ions of the trinuclear complex are all slightly distorted octahedral geometries with hexacoordination [54]. Unlike the mononuclear complex [Co(salen)], the Co(II) ion is a distorted square planar geometry with tetracoordination [56]. Whereas the Co(II) ion of trinuclear complex [Co₃(salamo)₂(OAc)₂]. THF with parent Salamo ligand exhibits two different coordination geometries, the terminal Co(II) ions possess pentacoordinated square pyramidal geometries; nevertheless, the central Co(II) ion has a hexacoordinated octahedral geometry [59]. It is obvious that the eight Co(II) ions of an octanuclear Co(II) cluster $[Co_8(3-OHSalamo)_4(H_2O)_2X] \cdot 2H_2O \cdot 1.5CHCl_3 \cdot 0.5hexane (X = H_2O)_4(H_2O)_2X] \cdot 2H_2O \cdot 1.5CHCl_3 \cdot 0.5hexane (X = H_2O)_4(H_2O)_2X$ or EtOH) are all pentacoordinated. The geometries around four outer Co(II) ions (Co1, Co2, Co3 and Co4) are trigonal bipyramidal (τ = 0.788–0.862). One of the inner Co(II) ions (Co6) has an intermediate geometry between trigonal bipyramidal and square pyramidal (τ = 0.521), however, Co8 is square pyramidal (τ = 0.083) and Co5 and Co7 are distorted one (τ = 0.274, 0.308).



Figure 1. (a) Molecular structure and atom numberings of complex **1** with 30% probability displacement ellipsoids(hydrogen atoms are omitted for clarity); (b) Coordination polyhedron for Co(II) ion of complex **1**.

 $(L^1)^{2-}$ unit of complex 1 acts as a tetradentate agent through two phenolic oxygen and oxime nitrogen atoms, which are in the equatorial positions. The four N₂O₂ donor atoms of $(L^1)^{2-}$ unit are approximately coplanar, and the dihedral angle of N1–N2–O4 and N2–O1–O4 is about 0.58(2)°. The axial sites are filled up by two water molecules in a relatively large angle of O5-Co(II)-O6

(175.33(12)°). It is explicit that the bond distance Co1–O5 (2.141(2) Å) shows a more significant length than that of Co1–O6 (2.124(2) Å), and this reveals the varied coordination abilities of the two coordinated water molecules (Table 2). TheCo(II)ion of complex **1** is almost coplanar with the mean plane through the N₂O₂ core, diverging from the mean plane by 0.028 Å and the four donor atoms (N1, N2, O1 and O4) from their mean plane by 0.008, -0.008, -0.008 and 0.008 Å. Thus, the octahedral Co(II) center is composed of the N₂O₂ coordination sphere made up of (L¹)^{2–} unit in the equatorial plane and two coordinated water molecules. The seven-membered chelate ring (Co–N1–O2–C8–C9–O3–N2) in complex **1** is in a gauche conformation with the ethylene carbon atoms above the N₂O₂ coordination plane (C8, 0.502 Å and C9, 1.148 Å). The Co–O(phenolic) bonds of 2.083(3) Å and 2.062(3) Å and

plane (C8, 0.502 Å and C9, 1.148 Å). The Co–O(phenolic) bonds of 2.083(3) Å and 2.062(3) Å and Co–N(oxime) bonds of 2.088(4) Å and 2.123(4) Å are in conformity with the average bond lengths observed for the corresponding bonds in the Co(II) complexes that anchors tetradentate Salamo-type ligands [62].

Complex 1			
Co101	2.083(3)	Co106	2.123(2)
Co1–O4	2.061(3)	Co1-N1	2.087(4)
Co1–O5	2.141(2)	Co1-N2	2.123(4)
O4-Co1-O6	93.3(1)	O4-Co1-N1	176.4(1)
O4-Co1-N2	85.5(1)	O5-Co1-O6	175.3(1)
O5-Co1-N1	87.6(1)	O5-Co1-N2	87.6(1)
O6-Co1-N1	87.7(1)	O6-Co1-N2	92.9(1)
N1-Co1-N2	97.9(1)		
Complex 2			
Zn1–O1	1.957(3)	Zn1-05	2.004(3)
Zn1-06	1.977(3)	Zn1–N1	2.122(4)
Zn1–N2	2.086(4)	Zn2–O4	2.029(3)
Zn2–O5	2.047(3)	Zn2–O7	1.972(3)
Zn2–O8	2.037(4)	Zn2–O4i	2.003(3)
O1-Zn1-O5	95.8(1)	O1-Zn1-O6	111.4(2)
O1–Zn1–N1	88.8(1)	O1-Zn1-N2	118.6(2)
O5-Zn1-O6	93.0(1)	O5-Zn1-N1	172.2(1)
O5-Zn1-N2	84.5(1)	06-Zn1-N1	91.1(1)
O6-Zn1-N2	130.0(2)	N1-Zn1-N2	87.9(1)
O4-Zn2-O5	79.3(1)	O4-Zn2-O7	145.4(1)
O4-Zn2-O8	107.9(1)	O4-Zn2-O4i	77.8(1)
O5-Zn2-O7	97.1(1)	O5-Zn2-O8	91.5(1)
O5–Zn2–O4i	156.1(1)	O7-Zn2-O8	106.7(2)
O7-Zn2-O4i	97.9(1)	O8-Zn2-O4i	101.9(1)

Table 2. Selected bond distances (Å) and bond angles (°) for complexes 1 and 2.

Symmetry transformations used to generate equivalent atoms: i: 2 - x, 1 - y, -z.

The crystal structures of complex **1** were linked by intermolecular O5–H5B···O4, O6–H6A···O1, C8–H8B···O2 and C9–H9B···O3 hydrogen bonding and weaker $\pi \cdots \pi$ (Ph) stacking interactions existing between adjacent phenyl rings (Tables 3 and 4) [17], which perform a crucial role in constructing and stabilizing supramolecular structure. The oxygen O2 (O3) atoms of the N₂O₂ molecules are hydrogen bonded to the C8–H8B (C9–H9B) groups of another complex molecule linking adjacent complex molecules into an infinite 2D supramolecular structure (Figure 2) [63–67].

D-H···A	D-H	Н…А	D····A	D-H···A
1				
O5-H5B-O4	0.86	2.06	2.797(4)	145
O6-H6A-O1	0.87	2.00	2.746(4)	143
O6-H6B-O4	0.87	2.07	2.853(4)	151
C8-H8B-O2	0.97	2.34	3.069(5)	131
C9-H9A-O6	0.97	2.35	3.272(6)	159
C9-H9B-O3	0.97	2.54	3.420(5)	150
2				
O8-H8-O1	0.87(4)	1.85(5)	2.666(5)	156(4)
C8-H8B-O6	0.97	2.48	3.308(6)	143

Table 3. Hydrogen bonding interactions (Å, $^{\circ}$) for complexes 1 and 2.

Table 4. π – π stacking interactions (Å, °) for complex **1**.

Ring 1 Ring 2	α	DCC(Å)	CgI-prep(Å)	CgJ-prep(Å)
Cg3 Cg3	1.7(2)	3.999(2)	3.734(2)	-3.756(2)
Cg4 Cg4	2.25(19)	3.936(2)	3.663(2)	-3.657(2)

Symmetry codes: Cg3 and Cg4 for complex 1 are the centroids of atoms C1–C6 and C11–C16, respectively; α = dihedral angle between planes I and J; DCC = distance between ring centroids; CgI-perp = perpendicular distance of Cg(I) from ring J; CgJ-perp = perpendicular distance of Cg(J) from ring I.



Figure 2. View of the 2D supramolecular structure of complex 1 showing the O–H…O, O–H…Cl hydrogen bonding and π – π stacking interactions.

3.3. Crystal Structure of Complex 2

Complex **2** crystallizes in the triclinic system and *P*-1 space group. As shown in Figure 3, the structure of complex **2** is made up of four Zn(II) ions, two deprotonated $(L^2)^{3-}$ units (in the form of enol), two μ -acetate ions and two coordinated n-PrOH molecules, showing consistency with the analytical data. The terminal Zn(II) (Zn1) ion is pentacoordinated by two oxime nitrogen (N1 and N2) atoms and two phenoxo oxygen (O1 and O5) atoms of one deprotonated $(L^2)^{3-}$ unit, and one oxygen (O6) atom of one μ -acetate ion, displaying a slightly distorted trigonal bipyramidal coordination motif ($\tau = 0.704$) (Figure 3). Meanwhile, the other Zn(II) (Zn2) ion is pentacoordinated by three phenoxo oxygen (O4, O4i and O5) atoms of two tetradentate deprotonated $(L^2)^{3-}$ units, one carbonyl oxygen (O7) atom from the μ -acetate ion as well as one hydroxyl oxygen (O8) atom from one coordinated

n-Pr-OH molecule. The coordination geometry around the Zn(II) (Zn2) ion can be described as a slightly distorted square pyramidal coordination sphere ($\tau = 0.178$) (Figure 3). This tetranuclear Zn(II) complex is rare case for Salen- or Salamo-type complexes, showing that the complexation of 3-hydroxy Salamo-type ligands with Zn(II) acetate occurs cooperatively [57], unlike in the case of other substituted Salen- [32–34] or Salamo-type ligands [35,36]. In fact, this tetranuclear Zn(II) complex exhibits a similar structure to the Zn(II) complex previously reported [35]. The description of the tetranuclear structure is two [Zn(L²)(μ -OAc)Zn(n-PrOH)] units connected with two diphenoxy-bridges. In each of the units, the Zn1 center was coordinated via N₂O₂ donors. The central Zn2 was coordinated by three deprotonated μ -phenolic oxygen atoms in two [Zn(L²)] chelates and one oxygen atom of coordinated n-propanol molecule. The acetate ion was coordinated to two Zn(II) ions through Zn1–O–C–O–Zn2 bridge. Thus, the complex is composed of four five-coordinated Zn(II) centers, alike with the coordination geometries of Zn(II) ions in the literature predecent [57]. This is attributed to the difference in the bond lengths and angles between the central ion, and the coordination groups, as well as the distortions of the geometries of the Zn(II) centers.



Figure 3. (a) Molecular structure and atom numberings of complex **2** with 30% probability displacement ellipsoids (hydrogen atoms are omitted for clarity). (b) Coordination polyhedra for Zn1 and Zn2 ions of complex **2**.

3.4. IR Spectra

The FT-IR spectra of H_2L^1 and H_3L^2 and their corresponding complexes **1** and **2** exhibit various bands in the 4000–400 cm⁻¹ region. Figure 4 shows the most important FT-IR bands for H_2L^1 and H_3L^2 and complexes **1** and **2**.

In general, the O-H stretching frequency of Salen-type ligand appears at approximately 3433 cm^{-1} owing to the intramolecuar OH····N=C hydrogen bonding [59], the absorption commonly appears in the FT-IR spectrum as a broad or double band and occasionally, the band seems to be undetectable. Disappearance of the band is expected for the metal complexes as a result of the substitution reaction when the OH hydrogen is substituted or replaced by the metal ions, thus leading to the complex formation [60].

At 1613 and 1612 cm⁻¹, the free ligands H_2L^1 and H_3L^2 show typical C=N stretching bands, while complexes **1** and **2** exhibit the characteristic C=N bands at 1609 and 1604 cm⁻¹, respectively. Upon complexation, shifts to lower frequencies by ca. 4 and 8 cm⁻¹ [52] are observed in the C=N

stretching frequencies for complexes **1** and **2**, respectively, indicating a decrease in the C=N bond order owing to the effects of the coordinated bonds of Co(II) and Zn(II) ions with the lone pair of oxime nitrogen electrons [61]. As reported, the Ar-O stretching frequency in the 1216–1213 cm⁻¹ range appears as a strong band [60]. These bands occur at 1270 and 1264 cm⁻¹ for the ligands H_2L^1 and H_3L^2 , and at 1209 and 1203 cm⁻¹ for complexes **1** and **2**, respectively. The Ar-O stretching frequencies are shifted to a lower frequency, indicating that the Co(II)-O and Zn(II)-O bonds were formed between the Co(II) and Zn(II) ions and oxygen of phenolic group [61].

The typical absorption bands at 3413, 1643, and 519 cm⁻¹ in complex **1** are assigned to the coordinated water molecules as are substantiated by crystal structure. The IR spectrum of complex **2** shows the expected strong absorption band due to vO-H at ca. 3450 cm⁻¹, which is evident for the existence of n-propanol molecule.



Figure 4. Infrared spectra of: (a) H_2L^1 ; and (b) H_3L^2 , and their corresponding complexes 1 and 2.

3.5. UV-Vis Spectra

The absorption spectra of ligands H_2L^1 and H_3L^2 and their corresponding complexes 1 and 2 were determined in 5×10^{-5} mol·L⁻¹ ethanolic solution (Figure 5). Obviously, the absorption peaks of the ligands H_2L^1 and H_3L^2 differ from those of complexes 1 and 2 upon complexation. The electronic absorption spectrum of the Salamo-type ligand H_2L^1 consists of three relatively intense bands centered at 225, 268 and 325 nm (for H_3L^2 , 219, 270 and 321 nm), which may be assigned to the π - π * transitions of the phenyl of salicylaldehyde and the oxime group [58]. The absorption bands at 268 and 325 nm (for H_3L^2 , 270 nm) disappear from the UV-vis spectrum upon complexation of the ligand with the metal ions, and indicates that the oxime nitrogen atoms are involved in coordination. The phenyl of salicylaldehyde intraligand π - π transition is a little shifted to 236 and 214 nm in the corresponding complexes 1 and 2, respectively. Besides, the newly emerged band observed at 377 nm for complex 1 is assigned to the L \rightarrow M charge-transfer transition, which is typical of the transition metal complexes with N₂O₂ coordination spheres [68].



Figure 5. UV-vis spectra of: (a) H_2L^1 ; and (b) H_3L^2 , and their corresponding complexes 1 and 2.

Thermal stability studies were performed for complexes **1** and **2**. The TG curve of complex **1** occurs in two stages. The first stage is between 132 and 176 °C. The TG curve shows a 6.0% weight loss in this temperature range, which is roughly similar to the 5.8% value calculated for the loss of two coordinated water molecule from the outer coordination sphere of complex **1**. Then, the remaining solid residue was stable up to around 207 °C, after which the compound begins to decompose. At 800 °C, the TG curve shows an approximately 88.3% total mass loss, indicating the complete removal of the $(L^1)^{2-}$ unit. The main residual product was CoO, with a value of 11.7% (theoretical residual value was 12.1%).

The TG curve of complex **2** occurred in three stages. The first stage occurs in the 187–215 °C range. The TG curve indicates that the weight loss corresponding to this temperature range is 10.4%, which is roughly similar to the 10.1% value estimated for the loss of two coordinated n-PrOH molecules from the inner coordination sphere of complex **2**. The second stage starts from 256 °C with a weight loss of 9.7%, which corresponds to the loss of two μ -acetate (theoretical mass loss, 9.9%) ions. Finally, the third weight loss starts at around 283 °C, leading to the full decomposition of the compound. At 650 °C, the TG curve shows about 92.8% total mass loss, indicating the complete removal of the (L²)^{3–} unit. The main residual product was ZnO, with a value of 7.2% (theoretical residual value was 6.8%).

4. Conclusions

In conclusion, according to the confirmed data, two new complexes with the chemical formulae $[Co(L^1)(H_2O)_2]$ (1) and $[{Zn(L^2)(\mu-OAc)Zn(n-PrOH)}_2]$ (2) were synthesized and structurally characterized by IR, UV-Vis spectra, TG-DTA and X-ray crystallography analyses, where H_2L^1 and H_3L^2 are 4,6-dibromo-4',6'-dichloro-2,2'-[ethylenediyldioxybis(nitrilomethylidyne)]diphenol and 6-hydroxy-4'-chloro-2,2'-[ethylenediyldioxybis(nitrilomethylidyne)]diphenol, respectively. The asymmetric unit of complex 1 contains a $[CoL^1]$ unit with 2 axially coordinated water ligands completing the coordination sphere, showing slightly distorted octahedral coordination geometry, and form a 2D layered supramolecular structureby molecular hydrogen bond and π - π stacking interactions. Complex 2 is made up of four Zn(II)ions, two coordinated OAc⁻ ions, two completely deprotonated (L^2)³⁻ moieties and two coordinatedn-propanol molecules, while the Zn(II)ions have slightly distorted trigonal bipyramidal and square pyramidal geometries.

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