



Structural Characterization of Heterodinuclear Zn^{II}-Ln^{III} Complexes (Ln = Pr, Nd) with a Ring-Contracted H₂valdien-Derived Schiff Base Ligand

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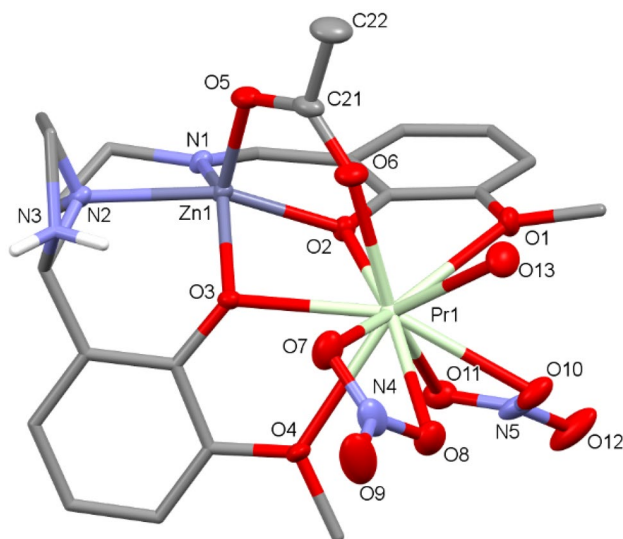
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Abstract

Synthesis and structural characterization of two heterodinuclear Zn^{II}-Ln^{III} complexes with the formula [ZnLn(HL)(μ-OAc)(NO₃)₂(H₂O)_x(MeOH)_{1-x}][NO₃ · n H₂O · n MeOH] [Ln = Pr (**1**), Nd (**2**)] and the crystal and molecular structure of [ZnNd(HL)(μ-OAc)(NO₃)₂(H₂O)] [ZnNd(HL)(OAc)(NO₃)₂(H₂O)](NO₃)₂ · n H₂O · n MeOH (**3**) are reported. The asymmetrical compartmental ligand (*E*)-2-(1-(2-((2-hydroxy-3-methoxybenzylidene)amino)-ethyl)imidazolidin-2-yl)-6-methoxyphenol (H₂L) is formed from *N*¹,*N*³-bis(3-methoxysalicylidene)diethylenetriamine (H₂valdien) through intramolecular amination, resulting in a peripheral imidazoline ring. The structures of **1–3** were revealed by X-ray crystallography. The smaller Zn^{II} ion occupies the inner N₂O₂ compartment of the ligand, whereas the larger and more oxophilic Ln^{III} ions are found in the outer O₂O₂' site.

Graphic Abstract

Synthesis and structural characterization of two heterodinuclear Zn^{II}-Ln^{III} complexes (Ln = Pr, Nd) bearing an asymmetrical compartmental ligand formed in situ from *N*¹,*N*³-bis(3-methoxysalicylidene)diethylenetriamine (H₂valdien) through intramolecular amination are reported.



Keywords Schiff base · Compartmental ligand · Chelate ligand · Heterodinuclear complex · Lanthanide · Zinc

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Introduction

Acyclic and macrocyclic Schiff base ligands are among the most extensively used ligands in coordination chemistry [1]. In general, Schiff bases can be readily prepared in good yields through condensation of primary amines with aldehyde or ketones. Owing to the ease of their synthesis, their versatility and ability to form stable complexes with almost all transition metals, Schiff base ligands have enormously contributed to the development of coordination chemistry and their transition metal complexes have been particularly important in bioinorganic chemistry, magnetochemistry, catalysis [2–4] and biomedical and related applications [5].

Polydentate Schiff base chelate ligands derived from condensation of 2-hydroxy-3-methoxybenzaldehyde (*o*-vanillin) or derivatives as aldehyde component with polyamines have been exploited for the synthesis of homo- and heterodinuclear complexes. These have attracted research attention because of interesting properties such as magnetism and luminescence [6–18]. *N*¹,*N*³-bis(3-methoxysalicylidene)diethylenetriamine (*H*₂valdien), which is obtained via Schiff base condensation of two equivalents of *o*-vanillin with diethylenetriamine, belongs to this class of ligands. After deprotonation of the phenol moieties, the resulting valdien²⁻ anion represents a compartmental ligand [19, 20], providing an inner binding site with an N₃O₂ donor set and an outer binding site with an outer O₂O₂' donor set. Whereas the inner compartment is expected to accommodate metal ions from the 3d row, the outer site may bind the more oxophilic lanthanide ions [6, 7, 21, 22]. Nevertheless, the inner compartment can also host lanthanide ions [8, 23–26]. Moreover, the *H*₂valdien ligand has also been encountered in a chelate-spacer-chelate bridging mode in dinuclear complexes with the aliphatic secondary amine linkages remaining unbound to the metal ions [27–30].

Herein, we report on the synthesis and structural characterization of two heterodinuclear Zn^{II}-Ln^{III} complexes with the general formula [ZnLn(HL)(μ-OAc)(NO₃)₂(H₂O)_x(MeOH)_{1-x}][NO₃ · *n* H₂O · *n* MeOH [Ln = Pr (**1**), Nd (**2**)], containing bridging acetate ions and the asymmetrical compartmental ligand (*E*)-2-(1-(2-((2-hydroxy-3-methoxybenzylidene)amino)-ethyl)imidazolidin-2-yl)-6-methoxy-phenol (*H*₂L) formed in situ from *H*₂valdien through isomerization by intramolecular amination formation, resulting in a peripheral imidazoline ring [27]. Such rearrangements are due to the reversibility of the Schiff base (imine) formation [31]. The rearranged ligand *H*₂L thus formed likewise represents a compartmental ligand but exhibits lower symmetry and a smaller inner compartment than the parent *H*₂valdien ligand. In addition,

the structure of the serendipitously discovered compound [ZnNd(HL)(μ-OAc)(NO₃)₂(H₂O)] [ZnNd(HL)(OAc)(NO₃)₂(H₂O)](NO₃)₂ · *n* H₂O · *n* MeOH (**3**) is described.

Experimental Section

General

The *H*₂valdien ligand was synthesised as described in the literature [23]. Zn(OAc)₂ · 2 H₂O (Fischer Scientific), Pr(NO₃)₃ · 6 H₂O and Nd(NO₃)₃ · 6 H₂O (Sigma Aldrich) were purchased and used as received. Methanol was of reagent grade. CHN microanalysis was carried out by Mikroanalytisches Labor Kolbe (Mülheim, Germany).

Synthesis of **1** and **2**

Zn(OAc)₂ · 2 H₂O (0.220 g, 1.0 mmol) dissolved in 10 mL of methanol was added to *H*₂valdien (0.371 g, 1.0 mmol) dissolved in 10 mL of acetonitrile and the mixture was stirred under reflux at 40 °C for 1 h. Subsequently, the yellow precipitate so formed was added to Pr(NO₃)₃ · 6 H₂O (0.435 g, 1.0 mmol) for **1** or Nd(NO₃)₃ · 6 H₂O (0.438 g, 1.0 mmol) for **2** in 40 mL of methanol and the reaction mixture was refluxed for a further 3 h. The solution was then filtered and the filtrate was set aside undisturbed at ambient temperature. Yellow–brown crystals of **1** and yellow crystals of **2** suitable for single-crystal X-ray diffraction were obtained after several days. Analytical data for the compounds are given below.

[ZnPr(HL)(μ-OAc)(NO₃)₂(H₂O)_{0.35}(MeOH)_{0.65}][NO₃ · 2 MeOH · H₂O (**1**; L²⁻ = C₂₀H₂₃N₃O₄²⁻): Yield: 0.580 g (0.62 mmol, 62%). Anal. calcd. for C_{24.65}H_{40.30}N₆O₁₉PrZn (*M* = 931.00 g mol⁻¹): C 31.8, H 4.4, N 9.0%; found: C 31.9, H 4.3, N 9.2%. MS(ESI⁺): *m/z* [H₃L]⁺ calcd. for C₂₀H₂₆N₃O₄⁺ 372.2, found 372.2, [Zn(HL)]⁺ calcd. for C₂₀H₂₄N₃O₄Zn⁺ 434.1, found 434.1; IR(ATR): 1640 cm⁻¹ (C=N stretch).

[ZnNd(HL)(μ-OAc)(NO₃)₂(H₂O)_{0.75}(MeOH)_{0.25}][NO₃ · 3 MeOH (**2**; L²⁻ = C₂₀H₂₃N₃O₄²⁻): Yield: 0.570 g (0.60 mmol, 60%). Anal. calcd. for C_{25.24}H_{41.50}N₆NdO₁₉Zn (*M* = 942.64 g mol⁻¹): C 32.2, H 4.4, N 8.9%; found: C 32.1, H 4.3 N 9.2%. MS(ESI⁺): *m/z* [H₃L]⁺ calcd. for C₂₀H₂₆N₃O₄⁺ 372.2, found 372.2, [Zn(HL)]⁺ calcd. for C₂₀H₂₄N₃O₄Zn⁺ 434.1, found 434.1; IR(ATR): 1640 cm⁻¹ (C=N stretch).

Physical Methods

Energy-dispersive X-ray spectroscopy (EDX) was undertaken on a Hitachi S3500N scanning electron microscope using a Si(Li) Pentafet Plus detector from Oxford

Instruments GmbH with a 25 kV excitation voltage, 600 s measuring time and $100\times$ magnification from a fine powder sample sprinkled on a self-adhesive carbon guide tap. IR spectra were measured in the range $4000\text{--}400\text{ cm}^{-1}$ with a Bruker ALPHA Platinum-ATR FT-IR spectrometer. ESI mass spectra were recorded on a Q ExactiveTM Plus Orbitrap mass spectrometer (Thermo Scientific, Bremen, Germany).

X-ray Crystallography

The X-ray intensity data were collected on a Bruker AXS Kappa Mach3 APEXII diffractometer at $T = 100(2)\text{ K}$, using Mo- K_{α} radiation ($\lambda = 0.71073\text{ \AA}$) from an Incoatec $\text{I}\mu\text{S}$ microfocus X-ray source with Helios mirrors. The data were processed with SAINT [32] and absorption corrections were carried out with SADABS [33]. The crystal structures were solved with SHELXT [34] and refined with SHELXL-2018/3 [35]. Disordered parts of the structures were refined with appropriate geometrical restraints and using free variables for the occupancies (see supplementary crystallographic data). Carbon-bound hydrogen atoms were placed in geometrically calculated positions and refined using the appropriate riding model. Hydrogen atoms attached to nitrogen and oxygen were treated by semi-free refinement using appropriate distance restraints. Some solvate methanol and water hydrogen atoms could not be located in the final difference Fourier map and were therefore excluded from the structure refinement. The structure of **3** was refined as an inversion twin, resulting in a Flack x parameter of 0.440(19) [36].

Crystal data and refinement details for 1: $\text{C}_{25}\text{H}_{39.68}\text{N}_6\text{O}_{18.34}\text{PrZn}$, $M_r = 924.03$, monoclinic, $P2_1/n$, $Z = 4$, $a = 11.3498(15)\text{ \AA}$, $b = 14.8170(19)\text{ \AA}$, $c = 21.488(3)\text{ \AA}$, $\beta = 101.864(2)^\circ$, $V = 3536.5(8)\text{ \AA}^3$, $F(000) = 1870$,

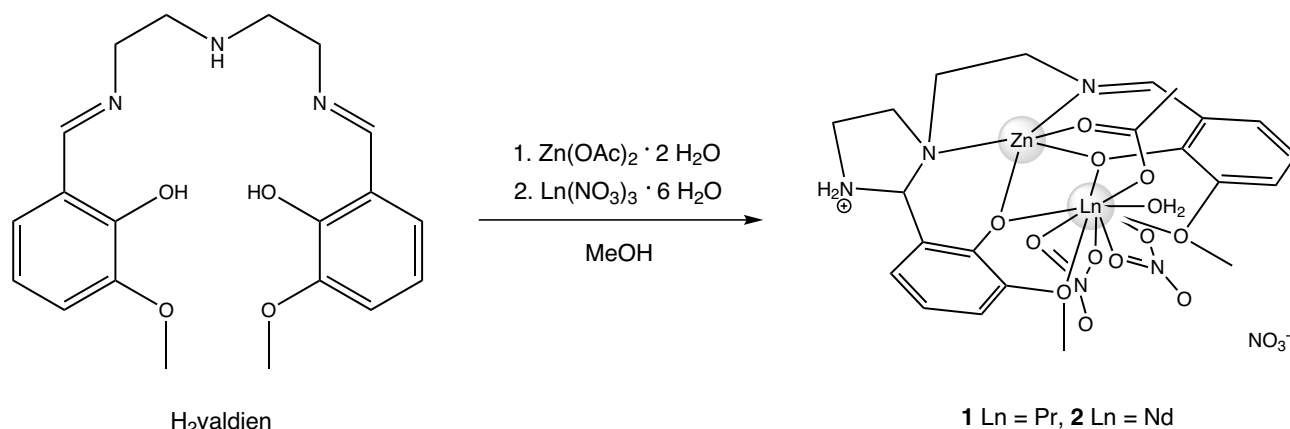
crystal size $0.223 \times 0.066 \times 0.031\text{ mm}$, $\rho_{\text{calcd}} = 1.735\text{ g cm}^{-3}$, $\mu = 2.125\text{ mm}^{-1}$, $2\theta_{\text{max}} = 62.22^\circ$, reflections collected/unique $104,376 / 11,339$ ($R_{\text{int}} = 0.0522$), parameters/restraints $512/16$, $R1 [I > 2\sigma(I)] = 0.0246$, $wR2$ (all data) = 0.0592, $S = 1.031$, $\Delta\rho_{\text{max}}/\Delta\rho_{\text{min}} = 0.65/-0.46\text{ e \AA}^{-3}$.

Crystal data and refinement details for 2: $\text{C}_{23.94}\text{H}_{35.26}\text{N}_6\text{NdO}_{18.90}\text{Zn}$, $M_r = 919.13$, monoclinic, $P2_1/n$, $Z = 4$, $a = 11.3439(13)\text{ \AA}$, $b = 14.7501(18)\text{ \AA}$, $c = 21.454(3)\text{ \AA}$, $\beta = 101.914(2)^\circ$, $V = 3512.4(7)\text{ \AA}^3$, $F(000) = 1848$, crystal size $0.086 \times 0.044 \times 0.024\text{ mm}$, $\rho_{\text{calcd}} = 1.736\text{ g cm}^{-3}$, $\mu = 2.231\text{ mm}^{-1}$, $2\theta_{\text{max}} = 62.14^\circ$, reflections collected/unique $153,810/11,217$ ($R_{\text{int}} = 0.1000$), parameters/restraints $529/85$, $R1 [I > 2\sigma(I)] = 0.0384$, $wR2$ (all data) = 0.0942, $S = 1.048$, $\Delta\rho_{\text{max}}/\Delta\rho_{\text{min}} = 1.48/-1.30\text{ e \AA}^{-3}$.

Crystal data and refinement details for 3: $\text{C}_{22}\text{H}_{27}\text{N}_6\text{NdO}_{18.05}\text{Zn}$, $M_r = 873.87$, monoclinic, Pn , $Z = 4$, $a = 11.2800(2)\text{ \AA}$, $b = 15.749(3)\text{ \AA}$, $c = 18.5316(8)\text{ \AA}$, $\beta = 102.908(2)^\circ$, $V = 3209.0(6)\text{ \AA}^3$, $F(000) = 1742$, crystal size $0.130 \times 0.060 \times 0.030\text{ mm}$, $\rho_{\text{calcd}} = 1.809\text{ g cm}^{-3}$, $\mu = 2.435\text{ mm}^{-1}$, $2\theta_{\text{max}} = 66.18^\circ$, reflections collected/unique $88,652/24,240$ ($R_{\text{int}} = 0.1126$), parameters/restraints $869/2$, $R1 [I > 2\sigma(I)] = 0.0705$, $wR2$ (all data) = 0.1700, $S = 1.025$, $\Delta\rho_{\text{max}}/\Delta\rho_{\text{min}} = 2.08/-1.48\text{ e \AA}^{-3}$.

Results and Discussion

The $\text{H}_2\text{valdien}$ ligand was prepared through Schiff base condensation of *o*-vanillin and diethylenetriamine in a 2:1 molar ratio [23]. Reaction with $\text{Zn}(\text{OAc})_2 \cdot 2\text{ H}_2\text{O}$ and, subsequently, with $\text{Ln}(\text{NO}_3)_3 \cdot 6\text{ H}_2\text{O}$ ($\text{Ln} = \text{Pr}$ or Nd) in methanol under reflux conditions afforded the heterodinuclear $\text{Zn}^{\text{II}}\text{--Ln}^{\text{III}}$ complexes **1** ($\text{Ln} = \text{Pr}$) and **2** ($\text{Ln} = \text{Nd}$), as depicted in Scheme 1. X-ray crystallography revealed that the $\text{H}_2\text{valdien}$ compartmental ligand underwent an



Scheme 1 Synthesis of **1** and **2**. The coordination site on Ln occupied by water or methanol in the solid-state is represented by water only in the diagram for the sake of clarity. Co-crystallized solvent molecules are not shown

isomerization through an intramolecular amination formation during the complexation reaction, resulting in an imidazolidine ring in the periphery. This phenomenon has been observed previously for the H₂valdien ligand and it was suggested that ring contraction optimizes binding of the Zn^{II} ion [27]. Some minor discrepancies between the sum formulae derived from elemental analysis of the bulk material as synthesized and those obtained from X-ray crystallography are ascribed to partial loss of co-crystallized solvents on drying before analysis. The presence of Zn and respectively, Pr and Nd in **1** and **2** was confirmed by EDX analysis (Fig. S1 in the supplementary material). The IR band at 1640 cm⁻¹ observed for both **1** and **2** (Figs. S2 and S3 in the supplementary material) is assigned to the imine C=N stretching vibration and agrees well with that reported for a heterodinuclear Zn^{II}-Ln^{III} complex having the reported formula “[ZnLn(HL)(NO₃)(S)](NO₃)”, where S = H₂O or C₂H₅OH, (CSD refcode: XODFOM) [27] and [Zn₄Dy₂(L)₂(L')₂(N₃)₂]Cl₂ · 2 H₂O (BIRXEI), [Zn₄Tb₂(L)₂(L')₂(Cl)₂][ZnN₃Cl₃] · 2 H₂O (BIRXOS), and [Zn₄Gd₂(L)₂(L')₂(Cl)₂][ZnN₃Cl₃] · 2 H₂O (BIRZAG) [37], containing the same rearranged compartmental ligand (herein abbreviated H₂L) and in the case of the latter three complexes the carbamate ligand L', derived from L by the absorption of CO₂ from the air in the presence of Zn^{II}. In the ESI⁺ mass spectra of **1** and **2** (Figs. S4-S7 in the supplementary material), the peaks at *m/z* 372.2 and 434.1 can be assigned to the fragment ions [H₃L]⁺ and [Zn(HL)]⁺, respectively.

Figure 1 depicts the molecular structures of the cationic complexes in **1** and **2** in the solid-state, as determined by X-ray crystallography. The structures of **1** and **2** were found to be isostructural. The Zn^{II} ion occupies the inner N₂O₂ compartment of the rearranged ligand, whereas the Ln^{III} ion

is situated in the outer O₂O₂ compartment. The intramolecular distance between the two metal ions is ca. 3.5 Å. The coordination sphere of the five-coordinate Zn^{II} ion is best described as square-pyramidal with the imine (N1) and amination nitrogen (N2) atoms and the bridging phenolate oxygen atoms of the chelate ligand in the basal plane and an acetate oxygen atom in the apical position. The geometry index τ_5 is 0.31 for **1** and 0.32 for **2** [38], indicating that the coordination geometry lies between square-pyramidal and trigonal-bipyramidal but closer to square-pyramidal (C_{4v} symmetry). The Ln^{III} ion is ten-coordinate with the two bridging phenolate and the two methoxy oxygen atoms of the chelate ligand occupying four coordination sites. The remaining positions are filled by two nitrate ions in a symmetrically bidentate coordination mode [39, 40], a water or alternatively a methanol oxygen atom (site of O13), and an oxygen atom of the μ -acetato- $\kappa O, O'$ ligand. The coordination geometry of the Ln^{III} ion can be best described as an approximate sphenocorona (C_{2v} symmetry), as determined by comparison with ideal polyhedra using continuous shape measures [41, 42]. As structural consequence of the intramolecular amination formation, the H₂L compartmental ligand adopts a bent conformation with the mean planes of the two aromatic rings being almost perpendicular (dihedral angle ca. 80°). A similar conformation of the ligand was found for XODFOM. In the crystal, the amination nitrogen atom N3 is protonated, making the complex cationic, and forms N–H···O hydrogen bonds to a methanol molecule of crystallisation and a nitrate counter ion, which balances the charge.

Serendipitously, we found a crystal in one crystallization batch of **2**, representing an unknown methanol solvate hydrate of a co-crystal (**3**) of [ZnNd(HL)(μ -OAc)(NO₃)₂(H₂O)]NO₃ and a structural isomer [ZnNd(HL)(OAc)

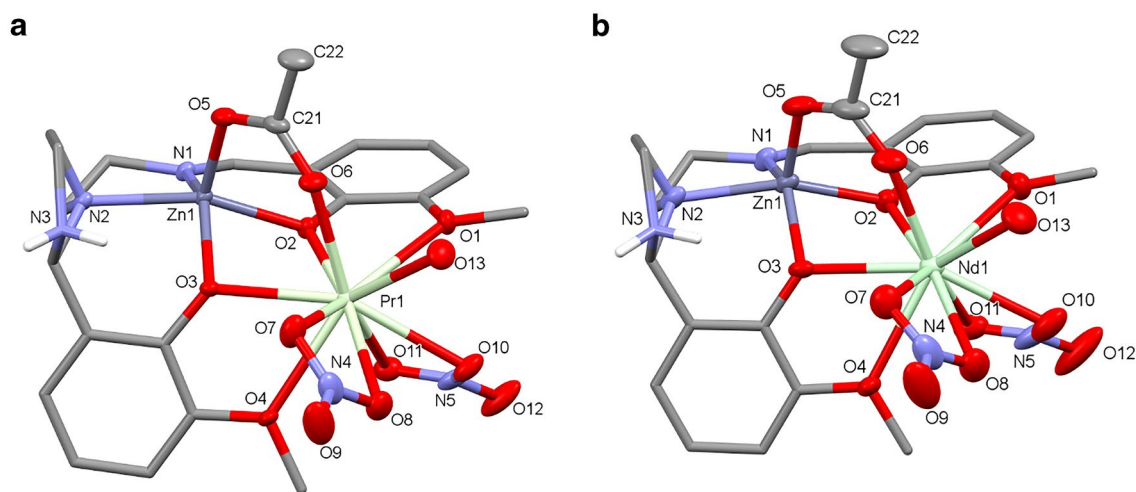


Fig. 1 Molecular structures of **1** and **2** in the crystal. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms (except for those attached to nitrogen), counter ions and solvent mol-

ecules are omitted for clarity. The site of O13 is occupied by water or methanol (not shown here for the sake of clarity) in the crystal

$(\text{NO}_3)_2(\text{H}_2\text{O})\text{NO}_3$ (Fig. 2). In the latter, a water molecule occupies the apical position at Zn^{II} and the acetato ligand binds solely to Nd^{III} in a symmetrical bidentate fashion. The coordination geometries of Nd^{III} and Zn^{II} are retained in the two isomers. In **3**, the geometry index τ_3 is 0.14 for Zn1 in $[\text{ZnNd}(\text{HL})(\mu\text{-OAc})(\text{NO}_3)_2(\text{H}_2\text{O})]^+$ and 0.43 for Zn1 in $[\text{ZnNd}(\text{HL})(\text{OAc})(\text{NO}_3)_2(\text{H}_2\text{O})]^+$.

The structures of **1** and **2** appear to be isostructural with the above-mentioned XODFOM, which has the reported molecular composition “[$\text{ZnLa}(\text{HL})(\text{NO}_3)_3(\text{S})$](NO_3)” ($\text{S} = \text{H}_2\text{O}$ or $\text{C}_2\text{H}_5\text{OH}$) [27], in which water and ethanol alternatively occupy one coordination site at La^{III} . However, whereas a $\mu\text{-acetato-}\kappa\text{O},\text{O}'$ ligand bridges the Zn^{II} and Ln^{III} in **1** and **2**, in XODFOM a bridging nitrate ion the Zn^{II} and La^{III} ions is reported. The reported N–O bond of the non-coordinating oxygen atom of the bridging nitrate ion in XODFOM is unusually long at 1.429(13) Å [39, 40], and the corresponding atomic displacement parameters are rather large, which may be a warning sign for incorrect atom type assignment [43–45]. Taking the reported synthetic route into account, the presence of a bridging acetate ligand in XODFOM is a possibility, since the precursor complex described as “[$\text{Zn}(\text{valdien})$] · 1.5 CH_3OH ”, which was not structurally characterized by X-ray crystallography, was prepared from $\text{H}_2\text{valdien}$ and $\text{Zn}(\text{OAc})_2 \cdot 2 \text{H}_2\text{O}$. Considering previous work by Naskar et al. [29], the constitution of the precursor complex might have been rather $[\text{Zn}_2(\text{H}_2\text{valdien})_2(\text{OAc})_2]$. Elemental analysis calcd. for $[\text{Zn}_2(\text{H}_2\text{valdien})_2(\text{OAc})_2]$ (C 53.40, H 5.50, N 8.49%) differs little from that reported for “[$\text{Zn}(\text{valdien})$] · 1.5 CH_3OH ” (C 53.10, H 5.80, N 8.30%) by Benetollo et al. [27]. We should note that the crystal structure of $[\text{Zn}(\text{valdien})] \cdot \text{CH}_3\text{OH}$ was published very recently [46], but an additional base (LiOH) was used in the synthesis

contrary to the synthesis of “[$\text{Zn}(\text{valdien})$] · 1.5 CH_3OH ” reported by Benetollo et al. The *syn-syn* bidentate bridging mode of the nitrate ion is known for inorganic nitrates [39, 47], but is rather unusual for organic or organometallic nitrate complexes [40]. In this connection, we note that the external N–O distances in the crystal structure with the CSD refcode ADURAV, reportedly containing two *syn-syn* bridging bidentate nitrate ligands between La^{III} and Zn^{II} , at 1.506(18) and 1.52(2) Å are also suspiciously long [48]. This coordination mode is, in contrast, well known for carboxylate ions [49]. The comparable C21–C22 bond lengths of 1.499(3) and 1.495(6) Å in **1** and **2**, respectively, and the corresponding atomic displacement parameters clearly support the presence of acetate ions at this site in XODFOM.

Conclusions

We have synthesized the heterodinuclear $\text{Zn}^{\text{II}}\text{-Ln}^{\text{III}}$ complexes **1** and **2** by successive treatment of the $\text{H}_2\text{valdien}$ compartmental ligand with $\text{Zn}(\text{OAc})_2 \cdot 2 \text{H}_2\text{O}$ and, respectively, $\text{Pr}(\text{NO}_3)_3 \cdot 6 \text{H}_2\text{O}$ and $\text{Nd}(\text{NO}_3)_3 \cdot 6 \text{H}_2\text{O}$, affording the asymmetrical, ring-contracted isomerized compartmental ligand H_2L from $\text{H}_2\text{valdien}$ in situ. Such a rearrangement of the $\text{H}_2\text{valdien}$ ligand, which has been described the literature, is enabled through the reversibility of the Schiff base condensation. Its occurrence in the formation of **1** and **2** can be ascribed to a better accommodation of the smaller Zn^{II} ion in the inner N_2O_2 binding site instead of the inner N_3O_2 site of the parent $\text{H}_2\text{valdien}$. As anticipated, the Ln^{III} ions are found in the outer $\text{O}_2\text{O}_2'$ compartment with counter ions and solvent molecules filling the remaining coordination sites of the ten-fold coordinated ions. Bond lengths, atomic displacement parameters

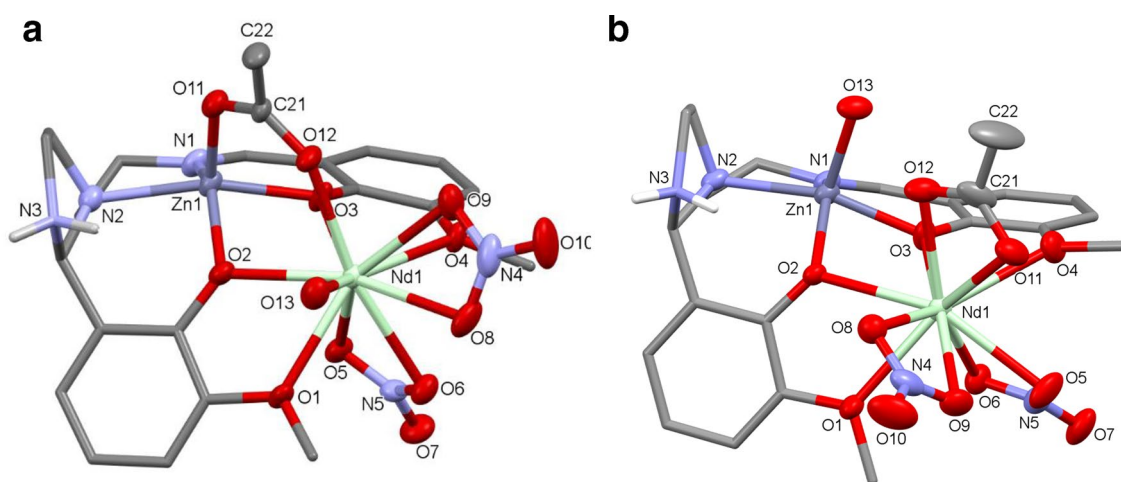


Fig. 2 Molecular structures of the two isomeric cations in the crystal structure of $[\text{ZnNd}(\text{HL})(\mu\text{-OAc})(\text{NO}_3)_2(\text{H}_2\text{O})]$ [$\text{ZnNd}(\text{HL})(\text{OAc})(\text{NO}_3)_2(\text{H}_2\text{O})$](NO_3) $_2 \cdot n \text{H}_2\text{O} \cdot n \text{MeOH}$ (**3**). Displacement ellipsoids

are drawn at the 50% probability level. Hydrogen atoms (except for those attached to nitrogen), counter ions and solvent molecules are omitted for clarity

and electron density maps resulting from the X-ray structural analysis provide clear evidence that the Zn^{II} and Ln^{III} ions in **1** and **2** are additionally linked by acetate anions in a *syn-syn* bridging mode rather than by nitrate anions, as has been proposed for similar structures. Detection of the [Zn(HL)]⁺ ion but no Ln^{III} adducts by ESI mass spectrometry suggests that the binding of Zn^{II} to the inner pocket of the ligand is, as expected, more stable than that of the Ln^{III} ions in the outer compartment. The crystal structure of **3** reveals that structural isomers of **2** occur.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s10870-021-00891-4>.

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Authors' Contributions Conceptualization: S.N. and S.K.; Data curation: R.G. and R.W.S.; Formal analysis: R.G. and R.W.S.; Funding acquisition: S.N.; Investigation: S.N. and R.G.; Methodology: R.G. and R.W.S.; Project administration: S.K. and R.W.S.; Resources: S.K., F.K. and R.G.; Supervision: S.K. and F.K.; Validation: R.G. and R.W.S.; Visualization: R.W.S.; Writing – original draft: R.W.S. and S.N.; Writing—review & editing: R.G. and R.W.S.

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Data Availability CCDC 2025504–2025506 contain the supplementary crystallographic data for **1–3**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

Code Availability Not applicable.

Declarations

Conflict of interest There are no conflicts of interest/competing interests to declare.

Ethical Approval Not applicable.

Consent to Participate Not applicable.

Consent for Publication All authors have seen the manuscript and agree to its publication.

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References

- Hernández-Molina R, Mederos A (2003) 1.19—Acyclic and macrocyclic Schiff base ligands. In: McCleverty JA, Meyer TJ (eds) *Comprehensive coordination chemistry II*. Pergamon, Oxford, pp 411–446
- Abu-Dief AM, Mohamed IMA (2015) A review on versatile applications of transition metal complexes incorporating Schiff bases. *Beni-Suef Univ J Basic Appl Sci* 4(2):119–133. <https://doi.org/10.1016/j.bjbas.2015.05.004>
- Dalia SA, Afsan F, Hossain MS, Khan M, Zakaria C, Zahan M, Ali M (2018) A short review on chemistry of schiff base metal complexes and their catalytic application. *Int J Chem Stud* 6(3):2859–2866
- Al Zoubi W, Ko YG (2017) Schiff base complexes and their versatile applications as catalysts in oxidation of organic compounds: part I. *Appl Organomet Chem* 31(3):e3574. <https://doi.org/10.1002/aoc.3574>
- More MS, Joshi PG, Mishra YK, Khanna PK (2019) Metal complexes driven from Schiff bases and semicarbazones for biomedical and allied applications: a review. *Mater Today Chem* 14:100195. <https://doi.org/10.1016/j.mtchem.2019.100195>
- Andruh M (2015) The exceptionally rich coordination chemistry generated by Schiff-base ligands derived from *o*-vanillin. *Dalton Trans* 44(38):16633–16653. <https://doi.org/10.1039/C5DT02661J>
- Pasatoiu TD, Tiseanu C, Madalan AM, Jurca B, Duhayon C, Sutter JP, Andruh M (2011) Study of the luminescent and magnetic properties of a series of heterodinuclear [Zn^{II}Ln^{III}] complexes. *Inorg Chem* 50(13):5879–5889. <https://doi.org/10.1021/ic200426w>
- Long J, Habib F, Lin P-H, Korobkov I, Enright G, Ungur L, Wernsdorfer W, Chibotaru LF, Murugesu M (2011) Single-molecule magnet behavior for an antiferromagnetically superexchange-coupled dinuclear dysprosium(III) complex. *J Am Chem Soc* 133(14):5319–5328. <https://doi.org/10.1021/ja109706y>
- Oyarzabal I, Artetxe B, Rodriguez-Dieguez A, Garcia J, Seco JM, Colacio E (2016) A family of acetato-diphenoxo triply bridged dimetallic Zn^{II}Ln^{III} complexes: SMM behavior and luminescent properties. *Dalton Trans* 45(23):9712–9726. <https://doi.org/10.1039/c6dt01327a>
- Liu C-M, Zhang D-Q, Su J-B, Zhang Y-Q, Zhu D-B (2018) Single-molecule magnet behavior of 1D coordination polymers based on DyZn₂(salen)₂ units and Pyridin-*N*-Oxide-4-Carboxylate: structural divergence and magnetic regulation. *Inorg Chem* 57(17):11077–11086. <https://doi.org/10.1021/acs.inorgchem.8b01653>
- Wong W-K, Liang H, Wong W-Y, Cai Z, Li K-F, Cheah K-W (2002) Synthesis and near-infrared luminescence of 3d–4f bimetallic Schiff base complexes. *New J Chem* 26(3):275–278. <https://doi.org/10.1039/b104175b>
- Echenique-Erandonia E, Zabala-Lekuona A, Cepeda J, Rodriguez-Dieguez A, Seco JM, Oyarzabal I, Colacio E (2018) Effect of the change of the ancillary carboxylate bridging ligand on the SMM and luminescence properties of a series of carboxylate-diphenoxido triply bridged dinuclear ZnLn and tetranuclear

- Zn₂Ln₂ complexes (Ln = Dy, Er). *Dalton Trans* 48(1):190–201. <https://doi.org/10.1039/c8dt03800g>
13. Fondo M, Corredoira-Vazquez J, Garcia-Deibe AM, Sanmartin-Matalobos J, Herrera JM, Colacio E (2017) Designing ligands to isolate ZnLn and Zn₂Ln complexes: field-induced single-ion magnet behavior of the ZnDy, Zn₂Dy, and Zn₂Er analogues. *Inorg Chem* 56(10):5646–5656. <https://doi.org/10.1021/acs.inorgchem.7b00165>
 14. Zhao S, Liu X, Wong W-Y, Lü X, Wong W-K (2014) Near infrared luminescent hexanuclear zinc–lanthanide prisms: synthesis, structure and luminescent properties. *Inorg Chim Acta* 414:160–164. <https://doi.org/10.1016/j.ica.2014.02.003>
 15. Liu C-M, Zhang DQ, Hao X, Zhu DB (2020) Zn₂Ln₂ complexes with carbonate bridges formed by the fixation of carbon dioxide in the atmosphere: single-molecule magnet behaviour and magnetocaloric effect. *Dalton Trans* 49(7):2121–2128. <https://doi.org/10.1039/c9dt04480a>
 16. Maeda M, Hino S, Yamashita K, Kataoka Y, Nakano M, Yamamura T, Kajiwaru T (2012) Correlation between slow magnetic relaxation and the coordination structures of a family of linear trinuclear Zn(II)–Ln(III)–Zn(II) complexes (Ln = Tb, Dy, Ho, Er, Tm and Yb). *Dalton Trans* 41(44):13640–13648. <https://doi.org/10.1039/c2dt31399e>
 17. Long J, Ivanov MS, Khomchenko VA, Mamontova E, Thibaud J-M, Rouquette J, Beaudhuin M, Granier D, Ferreira RAS, Carlos LD, Donnadieu B, Henriques MSC, Paixão JA, Guari Y, Larionova J (2020) Room temperature magnetoelectric coupling in a molecular ferroelectric ytterbium(III) complex. *Science* 367(6478):671. <https://doi.org/10.1126/science.aaz2795>
 18. Miroslaw B, Cristóvão B, Hnatejko Z (2018) Heterometallic Zn^{II}–Ln^{III}–Zn^{II} Schiff base complexes with linear or bent conformation—synthesis, crystal structures. *Luminescent and magnetic characterization*. *Molecules* 23(7):1761. <https://doi.org/10.3390/molecules23071761>
 19. Vigato PA, Tamburini S (2008) Advances in acyclic compartmental ligands and related complexes. *Coord Chem Rev* 252(18–20):1871–1995. <https://doi.org/10.1016/j.ccr.2007.10.030>
 20. Vigato PA, Peruzzo V, Tamburini S (2012) Acyclic and cyclic compartmental ligands: recent results and perspectives. *Coord Chem Rev* 256(11–12):953–1114. <https://doi.org/10.1016/j.ccr.2012.01.009>
 21. Liu C-M, Zhang D-Q, Hao X, Zhu D-B (2014) Trinuclear [Co^{III}₂–Ln^{III}] (Ln=Tb, Dy) single-ion magnets with mixed 6-Chloro-2-Hydroxypyridine and Schiff base ligands. *Chem Asian J* 9(7):1847–1853. <https://doi.org/10.1002/asia.201402001>
 22. Zhao L, Wu J, Xue S, Tang J (2012) A linear 3d–4f tetranuclear Co^{III}₂Dy^{III}₂ single-molecule magnet: synthesis, structure, and magnetic properties. *Chem Asian J* 7(10):2419–2423. <https://doi.org/10.1002/asia.201200548>
 23. Brunet G, Habib F, Korobkov I, Murugesu M (2015) Slow magnetic relaxation observed in dysprosium compounds containing unsupported near-linear hydroxo- and fluoro-bridges. *Inorg Chem* 54(13):6195–6202. <https://doi.org/10.1021/acs.inorgchem.5b00343>
 24. Bag P, Chakraborty A, Rouzières M, Clérac R, Butcher RJ, Chandrasekhar V (2014) Oxalato-bridged neutral octanuclear heterometallic complexes [Ln₄K₄(L)₄(μ-H₂O)₄(NO₃)₂(μ-Ox)] (Ln = Dy(III), Gd(III), Tb(III), Ho(III); LH₃ = N[CH₂CH₂N=CH–C₆H₃–2-OH–3-OMe]₃; Ox = (C₂O₄)²⁻): synthesis, structure, magnetic and luminescent properties. *Cryst Growth Des* 14(9):4583–4592. <https://doi.org/10.1021/cg500677t>
 25. Habib F, Brunet G, Vieru V, Korobkov I, Chibotaru LF, Murugesu M (2013) Significant enhancement of energy barriers in dinuclear dysprosium single-molecule magnets through electron-withdrawing effects. *J Am Chem Soc* 135(36):13242–13245. <https://doi.org/10.1021/ja404846s>
 26. Habib F, Lin P-H, Long J, Korobkov I, Wernsdorfer W, Murugesu M (2011) The use of magnetic dilution to elucidate the slow magnetic relaxation effects of a Dy₂ single-molecule magnet. *J Am Chem Soc* 133(23):8830–8833. <https://doi.org/10.1021/ja2017009>
 27. Benetollo F, Di Bernardo P, Tamburini S, Vigato PA, Zanonato P (2008) Mononuclear and polynuclear complexes with a side-off compartmental Schiff base. *Inorg Chem Commun* 11(3):246–251. <https://doi.org/10.1016/j.inoche.2007.11.022>
 28. Usman M, Arjmand F, Khan RA, Alsalmeh A, Ahmad M, Tabassum S (2017) Biological evaluation of dinuclear copper complex/dichloroacetic acid cocrystal against human breast cancer: design, synthesis, characterization, DFT studies and cytotoxicity assays. *RSC Adv* 7(76):47920–47932. <https://doi.org/10.1039/C7RA08262B>
 29. Naskar B, Modak R, Maiti DK, Drew MGB, Bauzá A, Frontera A, Das Mukhopadhyay C, Mishra S, Das Saha K, Goswami S (2017) A Schiff base platform: structures, sensing of Zn(II) and PPI in aqueous medium and anticancer activity. *Dalton Trans* 46(29):9498–9510. <https://doi.org/10.1039/C7DT01932G>
 30. Noor S, Goddard R, Kumar S, Ahmad N, Sabir S, Mitra P, Seidel RW (2018) On the chiral Z' = 2 crystal structure of [Cu₂(H₂valdien)₂](NO₃)₂ [H₂valdien = N^I, N³-bis(3-methoxy-salicylidene)diethylenetriamine]. *J Chem Crystallogr* 48(4):164–169. <https://doi.org/10.1007/s10870-018-0724-4>
 31. Belowich ME, Stoddart JF (2012) Dynamic imine chemistry. *Chem Soc Rev* 41(6):2003–2024. <https://doi.org/10.1039/C2CS15305J>
 32. SAINT (2012). Bruker AXS Inc., Madison, Wisconsin, USA
 33. SADABS (2012). Bruker AXS Inc., Madison, Wisconsin, USA
 34. Sheldrick GM (2015) SHELXT - integrated space-group and crystal-structure determination. *Acta Crystallogr A Found Adv* 71(Pt 1):3–8. <https://doi.org/10.1107/S2053273314026370>
 35. Sheldrick GM (2015) Crystal structure refinement with SHELXL. *Acta Crystallogr C Struct Chem* 71(Pt 1):3–8. <https://doi.org/10.1107/S2053229614024218>
 36. Flack H (1983) On enantiomorph-polarity estimation. *Acta Crystallogr A* 39(6):876–881. <https://doi.org/10.1107/S0108767383001762>
 37. Yin C-L, Hu Z-B, Long Q-Q, Wang H-S, Li J, Song Y, Zhang Z-C, Zhang Y-Q, Pan Z-Q (2019) Single molecule magnet behaviors of Zn₄Ln₂ (Ln = Dy^{III}, Tb^{III}) complexes with multidentate organic ligands formed by absorption of CO₂ in air through *in situ* reactions. *Dalton Trans* 48(2):512–522. <https://doi.org/10.1039/C8DT03849J>
 38. Addison AW, Rao TN, Reedijk J, van Rijn J, Verschoor GC (1984) Synthesis, structure, and spectroscopic properties of copper(II) compounds containing nitrogen–sulphur donor ligands; the crystal and molecular structure of aqua[1,7-bis(*N*-methylbenzimidazol-2'-yl)-2,6-dithiaheptane]copper(II) perchlorate. *J Chem Soc, Dalton Trans* 7:1349–1356. <https://doi.org/10.1039/DT9840001349>
 39. Addison CC, Logan N, Wallwork SC, Garner CD (1971) Structural aspects of co-ordinated nitrate groups. *Q Rev Chem Soc* 25(2):289–322. <https://doi.org/10.1039/QR9712500289>
 40. Morozov IV, Serezhkin VN, Troyanov SI (2009) Modes of coordination and stereochemistry of nitrate groups in organic and organometallic nitrates. *Russ Chem Bull* 58(12):2407–2417. <https://doi.org/10.1007/s11172-009-0336-4>
 41. Alvarez S, Alemany P, Casanova D, Cirera J, Lluell M, Avnir D (2005) Shape maps and polyhedral interconversion paths in transition metal chemistry. *Coord Chem Rev* 249(17):1693–1708. <https://doi.org/10.1016/j.ccr.2005.03.031>

42. M. Llunell, D. Casanova, J. Cirera, J. Bofill, P. Alemany, S. Alvarez, M. Pinsky, D. Avnir, SHAPE v. 2.1. Program for the calculation of continuous shape measures (CShM) of polygonal and polyhedral molecular fragments; CShM = 2.420 (1) and 2.433 (2).
43. Spek AL (2009) Structure validation in chemical crystallography. *Acta Crystallogr D Biol Crystallogr* 65(Pt 2):148–155. <https://doi.org/10.1107/S090744490804362X>
44. Spek AL (2018) What makes a crystal structure report valid? *Inorg Chim Acta* 470:232–237. <https://doi.org/10.1016/j.ica.2017.04.036>
45. Schwalbe CH (2018) Should we remediate small molecule structures? If so, who should do it? *Crystallogr Rev* 24(4):217–235. <https://doi.org/10.1080/0889311X.2018.1508209>
46. Noor S, Suda S, Haraguchi T, Khatoon F, Akitsu T (2021) Chiral crystallization of a zinc(II) complex. *Acta Cryst E* 77(5):542–546. <https://doi.org/10.1107/S2056989021003650>
47. Morozov IV, Serezhkin VN, Troyanov SI (2008) Modes of coordination and stereochemistry of the NO_3^- anions in inorganic nitrates. *Russ Chem Bull* 57(3):439–450. <https://doi.org/10.1007/s11172-008-0071-2>
48. Sreejith SS, Mohan N, Kurup MRP (2018) Experimental and theoretical analysis of a rare nitrate bridged 3d–4f complex containing LaZn_2 core synthesized from a Zn(II) metalloligand. *J Mol Struct* 1153:85–95. <https://doi.org/10.1016/j.molstruc.2017.10.008>
49. Deacon GB, Phillips RJ (1980) Relationships between the carbon-oxygen stretching frequencies of carboxylate complexes and the type of carboxylate coordination. *Coord Chem Rev* 33(3):227–250. [https://doi.org/10.1016/S0010-8545\(00\)80455-5](https://doi.org/10.1016/S0010-8545(00)80455-5)

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