Abstract

Synthesis and structural characterization of two heterodinuclear ZnII-LnIII complexes with the formula [ZnLn(HL)(µ-OAc)(NO3)2(H2O)x(MeOH)1-x]NO3 · nH2O · nMeOH [Ln = Pr (1), Nd (2)] and the crystal and molecular structure of [ZnNd(HL)(µ-OAc)(NO3)2(H2O)](NO3)2 · nH2O · nMeOH (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 N1,N3-bis(3-methoxysalicylidene)diethylenetriamine (H2valdien) through intramolecular aminal formation, resulting in a peripheral imidazoline ring. The structures of 1–3 were revealed by X-ray crystallography. The smaller ZnII ion occupies the inner N2O2 compartment of the ligand, whereas the larger and more oxophilic LnIII ions are found in the outer O2O2' site.

Graphic Abstract

Synthesis and structural characterization of two heterodinuclear ZnII-LnIII complexes (Ln = Pr, Nd) bearing an asymmetrical compartmental ligand formed in situ from N1,N3-bis(3-methoxysalicylidene)diethylenetriamine (H2valdien) through intramolecular aminal formation are reported.

Keywords Schiff base · Compartmental ligand · Chelate ligand · Heterodinuclear complex · Lanthanide · Zinc
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, magnetocatalysis, [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 homodinuclear complexes. These have attracted research attention because of interesting properties such as magnetism and luminescence [6–18].

Experimental Section

General

The H2valdien 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 (Mühlheim, 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 H2valdien (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.

\[ \text{[ZnPr(HL)(µ-OAc)(NO3)2(H2O)(NO3)2(H2O)0.75(MeOH)0.25]NO3} \]

Yield: 0.580 g (62%). Anal. calcd. for C23.65H38.30N6O19PrZn (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 C20H23N3O4Zn⁺ 434.1, found 434.1; IR(ATR): 1640 cm⁻¹ (C = N stretch).

\[ \text{[ZnNd(HL)(µ-OAc)(NO3)2(H2O)(NO3)2(H2O)0.75(MeOH)0.25]} \]

Yield: 0.508 g (60%). Anal. calcd. for C23.65H38.30N6NdO19Zn (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 C20H23N3O4Zn⁺ 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 x magnification from a fine powder sample sprinkled on a self-adhesive carbon guide tap. IR spectra were measured in the range 4000–400 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 \( T = 100(2) \) K, using Mo-Kα radiation (\( \lambda = 0.71073 \) Å) from an Incoatec μS 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 using free variables for the occupancies (see supplementary crystallographic data). Carbon-bound hydrogen atoms were placed in geometrically calculated positions and using free variables for the occupancies (see supplementary crystallographic data). Carbon-bound hydrogen atoms were placed in geometrically calculated positions and using free variables for the occupancies (see supplementary crystallographic data).

Crystal data and refinement details for 1: \( C_{25}H_{39.68}N_6O_{18.34}PrZn, M_r = 919.13, \) monoclinic, \( P2_1/n, Z = 4, a = 11.3439(13) \) Å, \( b = 14.7501(18) \) Å, \( c = 21.454(3) \) Å, \( \beta = 101.914(2) ^\circ, V = 3512.4(7) \) Å³, \( F(000) = 1870, \) crystal size \( 0.223 \times 0.066 \times 0.031 \) mm, \( \rho_{calc} = 1.736 \) g cm⁻³, \( \mu = 2.125 \) mm⁻¹, \( 2\theta_{max} = 62.22^\circ, \) reflections collected/unique 104,376 / 11,339 (\( R_{int} = 0.0522 \)), parameters/restraints 512/16, \( R(\{I > 2\sigma(I)\}) = 0.0246, wR2 (all data) = 0.0592, S = 1.031, \Delta \rho_{max}/\Delta \rho_{min} = 0.65/ -0.46 \) e Å⁻³.

Crystal data and refinement details for 2: \( C_{23.94}H_{35.26}N_6O_{18.90}Zn, M_r = 919.13, \) monoclinic, \( P2_1/n, Z = 4, a = 11.3439(13) \) Å, \( b = 14.7501(18) \) Å, \( c = 21.454(3) \) Å, \( \beta = 101.914(2) ^\circ, V = 3512.4(7) \) Å³, \( F(000) = 1848, \) crystal size \( 0.086 \times 0.044 \times 0.024 \) mm, \( \rho_{calc} = 1.736 \) g cm⁻³, \( \mu = 2.231 \) mm⁻¹, \( 2\theta_{max} = 62.14^\circ, \) reflections collected/unique 153,810/11,217 (\( R_{int} = 0.0000 \)), parameters/restraints 529/85, \( R(\{I > 2\sigma(I)\}) = 0.0384, wR2 (all data) = 0.0942, S = 1.048, \Delta \rho_{max}/\Delta \rho_{min} = 1.48/ -1.30 \) e Å⁻³.

Crystal data and refinement details for 3: \( C_{22}H_{27}N_6O_{18.05}NdZn, M_r = 873.87, \) monoclinic, \( Pn, Z = 4, a = 11.2800(2) \) Å, \( b = 15.749(3) \) Å, \( c = 18.5316(8) \) Å, \( \beta = 102.908(2) ^\circ, V = 3209.0(6) \) Å³, \( F(000) = 1742, \) crystal size \( 0.130 \times 0.060 \times 0.030 \) mm, \( \rho_{calc} = 1.809 \) g cm⁻³, \( \mu = 2.435 \) mm⁻¹, \( 2\theta_{max} = 66.18^\circ, \) reflections collected/unique 88,652/24,240 (\( R_{int} = 0.1126 \)), parameters/restraints 869/24, \( R(\{I > 2\sigma(I)\}) = 0.0246, wR2 (all data) = 0.1700, S = 1.025, \Delta \rho_{max}/\Delta \rho_{min} = 2.08/ -1.48 \) e Å⁻³.

Results and Discussion

The H₂valdien ligand was prepared through Schiff base condensation of \( o \)-vanillin and diethylenetriamine in a 2:1 molar ratio [23]. Reaction with Zn(OAc)₂ \cdot 2 H₂O and, subsequently, with Ln(NO₃)₃ \cdot 6 H₂O (Ln = Pr or Nd) in methanol under reflux conditions afforded the heterodi-nuclear Zn⁻⁻Ln⁻⁻ complexes 1 (Ln = Pr) and 2 (Ln = Nd), as depicted in Scheme 1. X-ray crystallography revealed that the H₂valdien compartmental ligand underwent an

![Scheme 1](image_url)
isomerization through an intramolecular aminal 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 ZnII 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 ZnII-LaIII complex having the reported formula “[ZnLa(HL)(NO3)2(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 ZnII. 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 ZnII ion occupies the inner N2O2 compartment of the rearranged ligand, whereas the LnIII 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 ZnII ion is best described as square-pyramidal with the imine (N1) and aminal 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 τ5 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 (C4v symmetry). The LnIII 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-κO,O’ ligand. The coordination geometry of the LnIII ion can be best described as an approximate sphenocorona (C2v symmetry), as determined by comparison with ideal polyhedra using continuous shape measures [41, 42]. As structural consequence of the intramolecular aminal 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 aminal 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 molecules 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.
(NO₃)₂(H₂O)]NO₃ (Fig. 2). In the latter, a water molecule occupies the apical position at ZnII and the acetato ligand binds solely to NdIII in a symmetrical bidentate fashion. The coordination geometries of NdIII and ZnII are retained in the two isomers. In 3, the geometry index τ₅ is 0.14 for Zn₁ in [ZnNd(HL)(µ-OAc)(NO₃)₂(H₂O)]⁺ and 0.43 for Zn₁ in [ZnNd(HL)(OAc)(NO₃)₂(H₂O)]⁺.

The structures of 1 and 2 appear to be isostructural with the above-mentioned XODFOM, which has the reported molecular composition “[ZnLa(HL)(NO₃)₃(S)](NO₃)” (S = H₂O or C₂H₅OH) [27], in which water and ethanol alternatively occupy one coordination site at LaIII. However, whereas a µ-acetato-κO,O’ ligand bridges the ZnII and LnIII in 1 and 2, in XODFOM a bridging nitrate ion the ZnII and LaIII 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 “[Zn2(H₂valdien)₂(OAc)₂]” is known for inorganic nitrates [39, 47], but is rather unusual for organic or organometallic nitrato 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 nitrate ligands between LaIII and ZnII, 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 C–C 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 ZnII-LnIII complexes 1 and 2 by successive treatment of the H₂valdien compartmental ligand with Zn(OAc)₂ · 2 H₂O and, respectively, Pr(NO₃)₃ · 6 H₂O and Nd(NO₃)₃ · 6 H₂O, affording the asymmetrical, ring-contracted isomerized compartmental ligand H₂L from H₂valdien in situ. Such a rearrangement of the H₂valdien 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 ZnII ion in the inner N₂O₂ binding site instead of the inner N₃O₂ site of the parent H₂valdien. As anticipated, the LnIII ions are found in the outer O₂O₂⁻ compartment with counter ions and solvent molecules filling the remaining coordination sites of the ten-fold coordinated ions. Bond lengths, atomic displacement parameters 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/10.1017/s10870-021-00891-4.

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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

1. 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

2. 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

3. 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

4. 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

5. 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

6. 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

7. Pasatouid TD, Tiseanu C, Madalan AM, Jurca B, Duhayon C, Suter 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/ic202426w

8. Long J, Habib F, Lin P-H, Korhokov I, Enright G, Ungur L, Werndsorfer 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/ja109706v

9. Oyarzabal I, Artetxe B, Rodriguez-Dieguez A, Garcia J, Seco JM, Colacio E (2016) A family of acetato-diphenoxido 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

10. 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 DyZn$_2$(salen)$_3$ 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

11. 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

12. Echenique-Errandonea 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 carboxylatediphenoxido triply bridged dinuclear ZnLa and tetrannuclear...
Zn\(_2\) Ln\(_3\) 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, Sammartini-Matalobos J, Herrera JM, Colacio E (2017) Designing ligands to isolate ZnLn and Zn\(_2\) Ln complexes: field-induced single-ion magnet behavior of the ZnDy, Zn\(_2\) Dy, and Zn\(_2\) Er analogues. Inorg Chem 56(10):5646–5656. https://doi.org/10.1021/acs.inorgchem.7b00165

14. Zhao S, Liu X, Wong W-Y, Lu 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.inoche.2014.02.003

15. Liu C-M, Zhang D-Q, Hao X, Zhu DB (2020) Zn\(_2\) Ln\(_3\) complexes with carbonate bridges formed by the fixation of carbon dioxide in the atmosphere: single-molecule magnetic 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, Kajiwara 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, 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, Beauduin 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, Cristovão B, Hnatejko Z (2018) Heterometallic Zn\(^{11}\)–Ln\(^{3}\)–Zn\(^{11}\) 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)\(_2\) μ-D2] complexes: design and magnetic properties. Inorg Chem 53(13):6195–6202. https://doi.org/10.1021/acs.inorgchem.5b00343

22. Bag P, Chakraborty A, Rouzières M, Clévac R, Butcher RJ, Chandrasekhar V (2014) Oxalato-bridged neutral octanuclear heterometallic complexes [Ln\(_2\) (κ\(_3\)-κ\(_3\)-μ-H\(_2\)O\(_2\))(NO\(_3\))\(_2\)](μ-OMe)\(_2\) (Ln = Dy(III), Gd(III), Tb(III), Ho(III)); LH\(_3\) = N\(_2\)C\(_2\)H\(_4\)N\(_2\)C\(_2\)H\(_4\)N\(_2\)CH\(_2\)CH\(_2\)OH-3-OME); ox = (C\(_3\)O\(_2\))\(_3\); synthesis, structure and magnetic properties. Crystal Growth Des 14(9):4583–4592. https://doi.org/10.1021/cg500677t

23. 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

24. Bag P, Chakraborty A, Rouzières M, Clévac R, Butcher RJ, Chandrasekhar V (2014) Oxalato-bridged neutral octanuclear heterometallic complexes [Ln\(_2\) (κ\(_3\)-κ\(_3\)-μ-H\(_2\)O\(_2\))(NO\(_3\))\(_2\)](μ-OMe)\(_2\) (Ln = Dy(III), Gd(III), Tb(III), Ho(III)); LH\(_3\) = N\(_2\)C\(_2\)H\(_4\)N\(_2\)C\(_2\)H\(_4\)N\(_2\)CH\(_2\)CH\(_2\)OH-3-OME); ox = (C\(_3\)O\(_2\))\(_3\); synthesis, structure and magnetic properties. Crystal 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
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, Sada 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) metallogligand. 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 carboxylato complexes and the type of carboxylate coordination. Coord Chem Rev 33(3):227–250. https://doi.org/10.1016/S0010-8545(00)80455-5

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