

Synthesis and structure of mixed metal Zn₃Ni₂-complexes of tetradentate Schiff bases

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Abstract : The nickel(II) tetradentate Schiff base complexes, Ni(SALEN), Ni(S-BrSALEN), Ni(SALPN_x) and Ni(SALPN_y) underwent facile reactions with zinc perchlorate hexahydrate, Zn(ClO₄)₂·6H₂O resulting in excellent complex formations. Compounds of formula [$\{ZnL\}_2Zn(H_2O)_2\}(ClO_4)_2 \cdot 2NiL \cdot \frac{1}{2}H_2O$ (where L = *N,N'*-ethylenebis(salicylideneiminato) dianion, (SALEN)²⁻; *N,N'*-ethylenebis(5-bromosalicylideneiminato) dianion, (5-BrSALEN)²⁻; *N,N'*-1,3-propylenebis(salicylideneiminato) dianion, (SALPN_x)²⁻; *N,N'*-1,2-propylenebis(salicylideneiminato) dianion, (SALPN_y)²⁻] were isolated as powdery solid materials and were characterized by spectroscopic methods and X-ray crystallographic structure analysis. Single crystal X-ray crystallographic structure analysis performed on [$\{Zn(SALEN)\}_2Zn(H_2O)_2\}(ClO_4)_2 \cdot 2Ni(SALEN) \cdot \frac{1}{2}H_2O$ (1) showed it to crystallize in monoclinic space group, *C2/c* with *Z* = 4, and *a* = 28.527(2), *b* = 10.175 (1), *c* = 24.161(2) Å, β = 111.892(5)°. The geometric centre of the molecule lies on a crystallographic two-fold axis. Two of the three Zn^{II} ions are in square planar coordination with two SALEN dianions whereas the centrally located Zn^{II} ion is coordinated to two water molecules and to four oxygen atoms of the two Zn(SALEN) fragments formed *in situ* during the course of the reaction, in a distorted octahedral fashion showing the presence of Zn^{II} ions in two different coordination environments in a single complex. The structure is completed with two perchlorate ions, two Ni(SALEN) molecules and there is only half water molecule per formula unit.

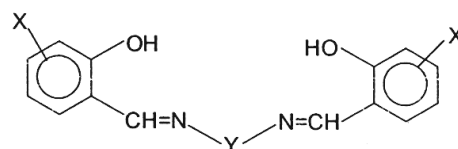
Keywords : Schiff base, dibasic tetradentate, hexadentate chelation, mixed-metal, nickel-zinc complexes, crystal structure.

Introduction

Tetradentate Schiff base (salen type) ligands and complexes play a profound role in homogeneous catalysis¹. In the past decade or so salen structures are found to be highly useful components of various supramolecular materials² which are multimetallic systems useful for catalytic operations³, macrocyclic compounds⁴ and new templating systems⁵. For all these purposes, it is important to understand and make effective use of the reactivity and stability characteristic of the salen building blocks monitoring the material properties. The most successful and usual approach to the synthesis of homo- and heteronuclear complexes is the use of suitable polydentate ligands with more than two coordination sites⁶⁻¹⁰. Another strategy that has been successfully exploited is the use of metal complexes as ligands i.e. metal complexes containing potential bonding groups for another metal or metal complexes with empty bonding sites¹¹⁻¹⁶. We recently have reported¹⁷ the isolation of mixed metal tetradentate Schiff base complexes containing Cu₂Zn-tri-

angular unit. Tetradentate Schiff base complexes of nickel(II) on the other hand are found to be undergoing facile reactions with zinc perchlorate hexahydrate, Zn(ClO₄)₂·6H₂O leading to the isolation of unique supramolecular aggregates with Zn₃-trinuclear unit present in them. Spectroscopic data and the results of single crystal X-ray crystallographic structure analysis performed on one of the compounds,

$[\{Zn(SALEN)\}_2Zn(H_2O)_2] \cdot 2Ni(SALEN) \cdot \frac{1}{2}H_2O$ are presented here.



- X = H; Y = -CH₂-CH₂- : SALENH₂
X = 5-Br; Y = -CH₂-CH₂- : 5-BrSALENH₂
X = H; Y = -CH₂-CH₂-CH₂- : SALPN_xH₂
X = H; Y = -CH₂-CH- : SALPN_yH₂
 |
 CH₃

Experimental

The tetradentate Schiff bases (TSBH₂) were prepared by the usual method of condensation of salicylaldehyde/5-bromosalicylaldehyde with ethylenediamine/1,3-diaminopropane/1,2-diaminopropane in 2 : 1 molar ratios in refluxing ethanol. The nickel(II) tetradentate Schiff base complexes [*N,N'*-ethylenebis(salicylaldiminato)]nickel(II), Ni(SALEN); [*N,N'*-ethylenebis(5-bromosalicylaldiminato)]nickel(II), Ni(5-BrSALEN); [*N,N'*-1,3-propylenebis(salicylaldiminato)]nickel(II), Ni(SALPN_x) and [*N,N'*-1,2-propylenebis(salicylaldiminato)]nickel(II), Ni(SALPN_y) were prepared as reported earlier^{18,19}. Crystalline zinc(II) perchlorate hexahydrate, Zn(ClO₄)₂·6H₂O (Aldrich) and all other chemicals were of reagent grade and was used as purchased. Solvents were dried and distilled before use. Microanalysis of C, H, N were performed on a Perkin-Elmer-2400 Series II CHN analyzer. Metal contents were estimated on a Perkin-Elmer atomic absorption spectrometer. Electronic spectra were recorded on a Shimadzu UV-Vis 1601 Spectrophotometer. A Perkin-Elmer FT IR Paragon 1000 Spectrometer was used to record the infrared spectra.

X-Ray crystallography :

A crystal of about 0.30 × 0.20 × 0.20 mm size of (1) was mounted in a sealed glass capillary and measured at room temperature on a Nonius Kappa CCD-diffractometer using graphite monochromated MoK_α radiation (λ = 0.71073 Å). The structure was solved by direct methods using SIR92²⁰ and structure refinement on *F*² was carried out with SHELXL97²¹. For molecular graphics ORTEP III²² was used.

Preparation of the heterometallic complexes :

Zn(ClO₄)₂·6H₂O (3.0 mmol) dissolved in 30 ml acetonitrile was added to the Ni(TSB) complexes (3.0 mmol) dissolved in 30 ml dichloromethane under constant stirring at room temperature and the mixtures were then refluxed for two hours. Filtered off when hot, the clear filtrate on cooling yielded dark crystalline solid which were collected by filtration, washed successively with acetonitrile and dichloromethane and finally dried *in vacuo*.

Caution! Perchlorate salts and perchlorate salts of metal complexes are potentially explosive. Although not

experienced any incident they should be handled with extreme care.

Results and discussion

Ni(SALEN) dissolved in dichloromethane showed facile reaction with Zn(ClO₄)₂·6H₂O dissolved in acetonitrile at room temperature. The reaction mixture was allowed to reflux for 2 h to ensure completion of the reaction whereby the relatively large complex molecule comprising of three zinc and two nickel atoms, [{Zn(SALEN)}₂Zn(H₂O)₂](ClO₄)₂·2Ni(SALEN)·½H₂O (1) got stabilized. Reactions of Ni(5-BrSALEN), Ni(SALPN_x) and Ni(SALPN_y) with Zn(ClO₄)₂·6H₂O as well yielded similar complexes, [{Zn(5-BrSALEN)}₂Zn(H₂O)₂](ClO₄)₂·2Ni(5-BrSALEN)·½H₂O (2), [{Zn(SALPN_x)}₂Zn(H₂O)₂](ClO₄)₂·2Ni(SALPN_x)·½H₂O (3) and [{Zn(SALPN_y)}₂Zn(H₂O)₂](ClO₄)₂·2Ni(SALPN_y)·½H₂O (4).

The products were isolated as dark red to pinkish red powdery solid. The reaction of Ni(SALPN_x) with Zn(ClO₄)₂·6H₂O was particularly found to be slow at room temperature. Appreciable reaction however took place when allowed to reflux for 2 h yielding analogous product. On the otherhand, Ni(SALHN) (SALHNH₂ = tetradentate Schiff base derived from salicylaldehyde and 1,6-diaminohexane) when brought into reaction with Zn(ClO₄)₂·6H₂O under identical conditions, no reaction took place at all suggesting that the longer the chain length of the diamine deriving the tetradentate Schiff base the lesser is the prospect of such reaction to take place.

Yields, m.p., results of elemental analysis and spectroscopic data of the complexes are presented in Table 1 and Table 2.

Infrared spectra :

The infrared spectra (IR) of the tetradentate Schiff bases and their metallic complexes has long been the subject of much discussion²³ which with some deviations are grossly applicable in these complexes also.

The IR spectra showed strong absorptions at 1630–1620 cm⁻¹ assignable to ν(C=N) vibrations²⁴ which remained nearly unchanged from that observed for the precursor complexes Cu(TSB) (dianion of the tetradentate

Table 1. Analytical and physical data of the complexes

Complex/ (colour, yield)	M.p. (°C) (dec.)	Analysis (%) : Found/(Calcd.)			
		C	H	N	Ni
[{Zn(SALEN)} ₂ Zn(H ₂ O) ₂](ClO ₄) ₂ . 2Ni(SALEN).½H ₂ O (1) (Orange red, 47%)	282	47.14 (47.37)	3.68 (3.79)	7.08 (6.94)	7.10 (7.24)
[{Zn(5-BrSALEN)} ₂ Zn(H ₂ O) ₂](ClO ₄) ₂ . 2Ni(5-BrSALEN). ½H ₂ O (2) (Red, 42%)	> 300	39.82 (39.66)	2.89 (2.96)	5.63 (5.78)	6.17 (6.08)
[{Zn(SALPN _x)} ₂ Zn(H ₂ O) ₂](ClO ₄) ₂ . 2Ni(SALPN _x).½H ₂ O (3) (Pale red, 33%)	212	47.94 (47.70)	3.94 (3.88)	6.95 (6.84)	7.26 (7.17)
[{Zn(SALPN _y)} ₂ Zn(H ₂ O) ₂](ClO ₄) ₂ . 2Ni(SALPN _y).½H ₂ O (4) (Crimson red, 44%)	263	47.07 (47.70)	3.72 (3.88)	6.73 (6.84)	6.98 (7.17)

Schiff bases).

The $\nu(\text{C-O})$ phenolic bands appeared around 1340–1300 cm^{-1} were shifted more appreciably than in Cu(TSB) precursor complexes. The shift was again more appreciable compared to what were observed for free Schiff bases and was attributed to the coordination of phenolic oxygen to both the metal centres^{7,25} indicative of a strong

reduction of the C–O bond order due to complexation. Besides there were bands due to $\nu(\text{C=C})$, $\nu(\text{C-C})$ and $\nu(\text{C-N})$ which complicated the exact assignments of all the bands. The medium but sharp bands at 770–750 cm^{-1} were assigned as the out-of-plane C–H deformation of the phenyl ring. Presence of strong bands in the range 1110–1080 cm^{-1} (antisymmetric stretch) and medium but sharp bands at 627–621 cm^{-1} (antisymmetric bend) indicated the presence of uncoordinated perchlorate ion^{26,27}. The $\nu(\text{M-N})$ and $\nu(\text{M-O})$ vibrations were observed at 540–520 cm^{-1} and 480–460 cm^{-1} respectively.

Electronic spectra :

The electronic spectra of the Zn₃Ni₂ complexes (**1-4**) showed two intense bands in the near ultraviolet region assignable to $\pi \rightarrow \pi^*$ and ligand (σ_{L}) \rightarrow metal (e_{g}) charge transfer transitions^{28,29} respectively. Both the bands appeared at shorter wavelengths (at 270–280 nm and 320–340 nm) compared to those observed for the precursor tetradentate Schiff base complexes of nickel(II). The complexes (**1-4**) showed medium to low intensity d-d bands (~ 540 nm) at nearly the same wavelength as those of the precursor complexes assignable to the $^1A_1 \rightarrow ^1B_1$ transitions³⁰.

Crystal structure analysis of [{Zn(SALEN)}₂Zn(H₂O)₂](ClO₄)₂.2Ni(SALEN).½H₂O (1) :

The crystal turned out to belong to the monoclinic

Table 2. Electronic and IR (cm^{-1}) spectral data of the complexes

Complex	λ_{max} (nm) (log ϵ)	$\nu(\text{C=N})$	$\nu(\text{C-O})$ (phenolic)	$\nu_{\text{as}}(\text{ClO}_4^-)$	$\delta_{\text{as}}(\text{ClO}_4^-)$	$\delta(\text{C-H})$ (phenyl)	$\nu(\text{M-N})$	$\nu(\text{M-O})$
1	276(4.58), 351(4.18), 578(sh)	1629(vs), 1602(s)	1338(m)	1121(vs), 1091(s)	624(m)	770(s)	516(w,br)	474(m)
2	278(4.12), 367(4.10), 552(2.39)	1627(vs)	1320(m)	1108(vs)	626(m)	768(s)	542(w)	470(m)
3	273(4.20), 341(3.88), 408(3.42), 568(sh)	1628(vs)	1332(w)	1092(vs)	623(s)	756(vs)	539(m)	470(m)
4	273(4.34), 322(3.93), 405(sh), 533(sh)	1625(vs), 1601(vs)	1312(sh), 1288(s)	1110(vs), 1089(vs)	626(s)	761(s)	522(w)	467(m)

Table 3. Crystal data and structure refinement for complex (1)

Empirical formula	C ₆₄ H ₆₁ Cl ₂ N ₈ O _{18.5} Ni ₂ Zn ₃
Formula weight	1622.64
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	monoclinic
Space group	C2/c
Unit cell dimensions	
<i>a</i> (Å)	28.527(2)
<i>b</i> (Å)	10.175(1)
<i>c</i> (Å)	24.161(2)
β (°)	111.892(5)
Volume (Å ³)	6507.1(9)
<i>Z</i>	4
<i>D</i> _{calc} (mg m ⁻³)	1.656
Absorption coefficient (mm ⁻¹)	1.820
<i>F</i> (000)	3316
Crystal size (mm)	0.30 × 0.20 × 0.20
θ Range for data collection (°)	1.54 to 24.59
Limiting indices	-33 ≤ <i>h</i> ≤ 33, -11 ≤ <i>k</i> ≤ 11, -28 ≤ <i>l</i> ≤ 28
Reflections collected/unique	21866/5409 [<i>R</i> _{int} = 0.0663]
Completeness to $\theta = 24.59$	98.8%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.765 and 0.632
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	5409/70/490
Goodness-of-fit on <i>F</i> ²	1.076
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0648, <i>wR</i> ₂ = 0.1551
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.1254, <i>wR</i> ₂ = 0.1961
Largest difference peak and hole (e.Å ⁻³)	0.771 and -0.863

space group C2/c with *Z* = 4 and *a* = 28.527(2), *b* = 10.175(1), *c* = 24.161(2) Å, β = 111.892(5), *V* = 6507.1(9) Å³. Solution and refinement of the crystal structure revealed the composition of the crystal as [$\{Zn(SALEN)\}_2Zn(H_2O)_2\}(ClO_4)_2 \cdot 2Ni(SALEN)_2 \cdot \frac{1}{2}H_2O$ (1). The H₂O molecules in the complex molecule are assumed to stem from water traces in the solvents used for synthesis. The final *R*₁ value for the composition (1) is 0.0648.

The crystal structure of (1) consists of a trinuclear species [$\{Zn(SALEN)\}_2Zn(H_2O)_2\}(ClO_4)_2$, two Ni(SALEN) and $\frac{1}{2}H_2O$ molecules. Zn(2)²⁺ is coordi-

nated bidentally by two [Zn(1)(SALEN)] molecules and by two O(H₂O) atoms. Zn(2) lies on a crystallographic two-fold axis. The Zn coordination polyhedron defined by 2 × 2 O atoms of the [Zn(SALEN)] ligands and the two additional O (H₂O) ligands is a distorted octahedron (see Fig. 1). A simplified view of the molecule cation showing only the Zn centres and the coordination framework is shown in Fig. 2 and the stereoview of the molecule is shown in Fig. 3. The Zn-O(water) distance of 2.056(5) Å is in the range of distances found, e.g. in hexahydrate-zinc complexes^{31,32}. The two independent Zn-O(SALEN) distances (2.104(4) and 2.182(4) Å) differ by 0.078(4) Å. Similar differences have been observed²² where Gd-O(SALEN) distances range from 2.30 to 2.44 Å. The closeness of the bite of Zn(1)(SALEN) as bidentate ligand is the main cause of distortion (O(1)-Zn(2)-O(2), 69.97(17)°). O(2), O(2ⁱ), O(3), O(3ⁱ) are roughly forming a plane with O(1) and O(1ⁱ) atoms in axial positions, the coordination around Zn(2) ion is thus found to be distorted octahedral although the octahedral geometry around Zn ion is not very common^{33,34}. The average Ni-O (1.865(5) Å) and Ni-N (1.837(6) Å) distances in the neutral molecules are in the comparable ranges reported for other structures containing [Ni(SALEN)] molecules (Ni-O : 1.846(1)-1.863(1) Å; Ni-N : 1.842(1)-1.856(1) Å)^{16,35}. The perchlorate anion was two fold disordered. The disordered positions were located in successive difference Fourier map and refined.

The Fourier peak corresponding to lattice water O10 was rather feeble and hence it was decided to freely refine its site occupancy factor during refinement. The occupancy factor refined to the value 0.264 within the limits of standard deviation. The value was rounded to 0.25 and fixed during final stages of refinement. The final difference Fourier map showed no specific disorder for the atom but a rather feebly smeared electron density distribution in the region. Anisotropic refinement was not carried out for O10 as the displacement parameters may not represent true thermal motion in such situation. The water hydrogens were ignored. All other hydrogen atoms of the structure were geometrically fixed at chemi-

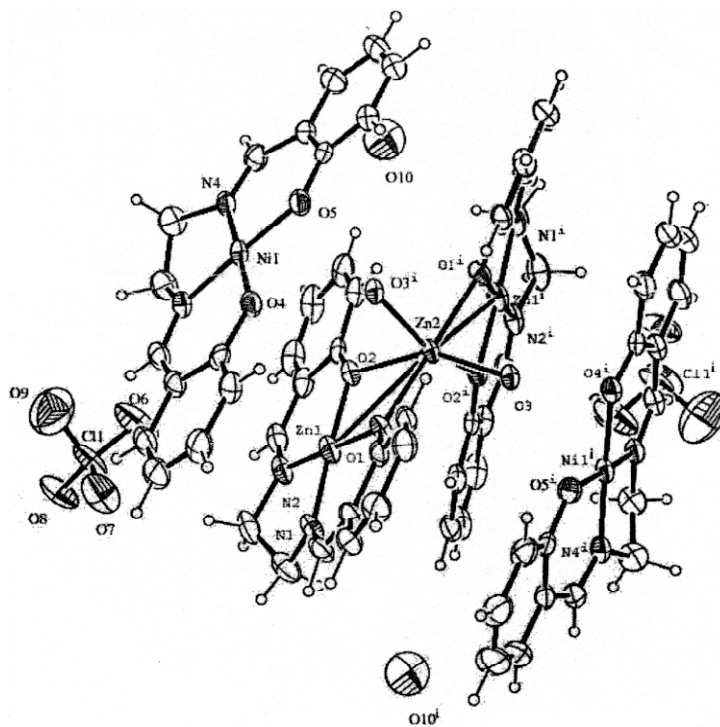


Fig. 1. An ORTEP drawing of the complex molecule $[\{Zn(SALEN)\}_2Zn(H_2O)_2](ClO_4)_2 \cdot 2Ni(SALEN) \cdot \frac{1}{2}H_2O$ (1).

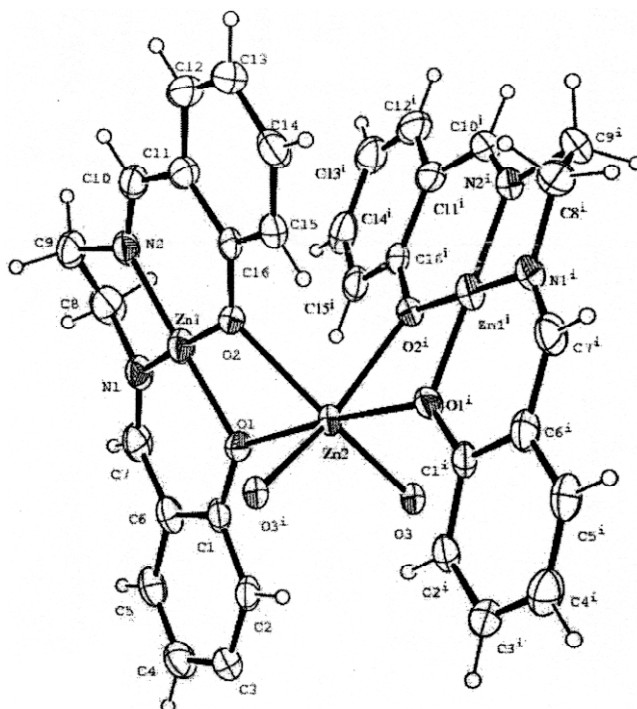


Fig. 2. Molecular structure of the cation $[\{Zn(SALEN)\}_2Zn(H_2O)_2]^{2+}$.

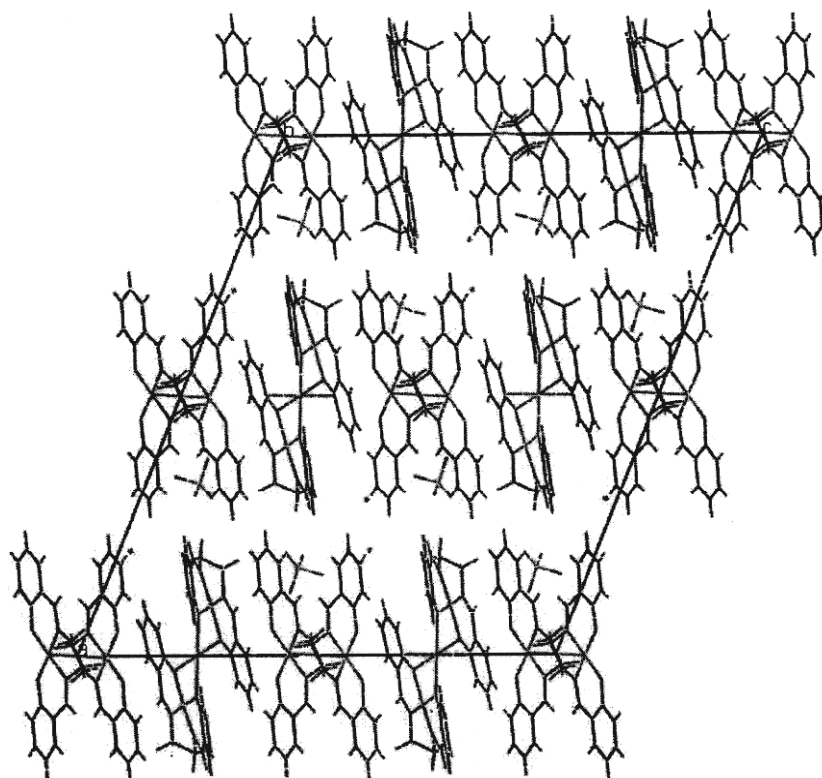


Fig. 3. Sterioview of the molecule (1).

Table 4. Selected bond lengths (Å) and bond angles (°) for complex (1)

Bond lengths :

N(1)-Zn(1)	1.835(7)	O(3)-Zn(2)	2.056(5)
N(2)-Zn(1)	1.825(6)	O(4)-Ni(1)	1.854(5)
N(3)-Ni(1)	1.838(6)	O(5)-Ni(1)	1.858(5)
N(4)-Ni(1)	1.836(6)	Cl(1)-O(6)	1.378(9)
O(1)-Zn(1)	1.848(4)	Cl(1)-O(8)	1.401(9)
O(1)-Zn(2)	2.104(4)	Cl(1)-O(9)	1.413(10)
O(2)-Zn(1)	1.840(5)	Cl(1)-O(7)	1.419(9)
O(2)-Zn(2)	2.182(4)	Zn(1)-Zn(2)	3.091(1)

Bond angles :

N(4)-Ni(1)-N(3)	86.4(3)	O(3)-Zn(2)-O(3)#1	109.6(3)
N(4)-Ni(1)-O(4)	178.2(2)	O(3)-Zn(2)-O(1)#1	87.70(18)
N(3)-Ni(1)-O(4)	93.9(2)	O(3)#1-Zn(2)-O(1)#1	89.75(18)
N(4)-Ni(1)-O(5)	94.1(2)	O(3)#1-Zn(2)-O(1)	87.70(18)
N(3)-Ni(1)-O(5)	177.6(2)	O(1)#1-Zn(2)-O(1)	175.6(2)
O(4)-Ni(1)-O(5)	85.6(2)	O(3)-Zn(2)-O(2)#1	89.77(17)
N(2)-Zn(1)-N(1)	85.6(3)	O(3)#1-Zn(2)-O(2)#1	151.67(18)
N(2)-Zn(1)-O(2)	96.1(3)	O(1)#1-Zn(2)-O(2)#1	69.97(17)
N(1)-Zn(1)-O(2)	177.2(2)	O(1)-Zn(2)-O(2)#1	113.64(18)
N(2)-Zn(1)-O(1)	179.4(2)	O(3)#1-Zn(2)-O(2)	89.77(17)
N(1)-Zn(1)-O(1)	94.7(3)	O(1)#1-Zn(2)-O(2)	113.64(18)

O(2)-Zn(1)-O(1)	83.6(2)	O(2)#1-Zn(2)-O(2)	81.1(2)
O(3)-Zn(2)-O(1)	89.75(18)		
O(1)-Zn(2)-O(2)	69.97(17)		
O(3)-Zn(2)-O(2)	151.68(18)		

Symmetry transformations used to generate equivalent atoms : #1-x+2, y, -z+3/2

cally meaningful positions and were given riding model refinement.

Supplementary data

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 791624. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 IEZ, UK (Fax : +44-1223-336-033; E-mail : deposit@ccdc.cam.ac.uk).

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