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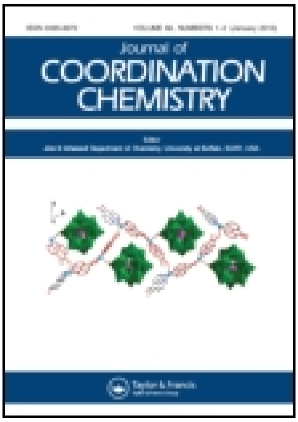

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Syntheses and structures of two $Ni^{II}Co^{II}Ni^{II}$ complexes of macrocyclic ligands

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Syntheses and structures of two $Ni^{II}Co^{II}Ni^{II}$ complexes of macrocyclic ligands

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Two new linear trinuclear complexes, $[Co(NiL^1)_2(SCN)_2]$ (**1**) and $[Co(NiL^2)_2(H_2O)_2](ClO_4)_2 \cdot 2C_2H_5OH$ (**2**), have been prepared by using $Co(ClO_4)_2 \cdot 6H_2O$ and two macrocyclic complex ligands NiL^1 and NiL^2. L^1 and L^2 are the doubly deprotonated forms of dimethyl 5,6,7,8,15,16-hexahydro-6,7-dioxodibenzo[1,4,8,11]tetraazabicyclo[12.4.0^{15,16}]13,18-dicarboxylate and dimethyl 5,6,7,8,15,16-hexahydro-15-methyl-6,7-dioxodibenzo[1,4,8,11] tetraazacyclotetradecine-13,18-dicarboxylate, respectively. X-ray single crystal analyses reveal the coordination geometries around Ni(II) in both **1** and **2** are identical and slightly distorted square planar with N_4 donors; all Ni–N bonds in the two complexes are very short. The Co(II) ions are at the centers of the trinuclear complexes and have distorted octahedral coordination geometries of O_4N_2 donors in **1** and an O_6 in **2**. $\pi \cdots \pi$ interactions involving aromatic and non-aromatic π-systems join the trinuclear entities to form 2-D layers in the crystals of **1** and **2**.

Keywords: Synthesis; Crystal structure; $\pi \cdots \pi$ Interaction; $Ni^{II}Co^{II}Ni^{II}$ trinuclear complex; Macrocyclic complex ligand

1. Introduction

Coordination chemistry of macrocyclic compounds has received considerable interest owing to its relationship to biology, medicine, and chemical techniques [1–4]. The ‘‘complex as ligand’’ method is one of the most important approaches for preparing polynuclear species [5, 6] and is especially viable to produce heterometallic multinuclear complexes. In this contribution, two complexes of macrocyclic oxamido Schiff bases, NiL^1 and NiL^2 (scheme 1), were used as ‘‘complex ligands’’ to synthesize two new linear $Ni^{II}Co^{II}Ni^{II}$ trinuclear complexes, $[Co(NiL^1)_2(SCN)_2]$ (**1**) and $[Co(NiL^2)_2(H_2O)_2](ClO_4)_2 \cdot 2C_2H_5OH$ (**2**). L^1 and L^2 denote the doubly deprotonated forms of dimethyl 5,6,7,8,15,16-hexahydro-6,7-dioxodibenzo[1,4,8,11]tetraazabicyclo[12.4.0^{15,16}]-13,18-dicarboxylate and dimethyl 5,6,7,8,15,16-hexahydro-15-methyl-6,7-dioxodibenzo[1,4,8,11]-tetraazacyclotetradecine-13,18-dicarboxylate, respectively. Linear trinuclear Ni-Co-Ni complexes are few [7–15]. Compound **1** is the first polynuclear complex of NiL^1 and **2** is the third polynuclear complex of NiL^2 [16, 17]. Both NiL^1 and NiL^2 showed DNA cleavage activity [18]. Such complex ligands can

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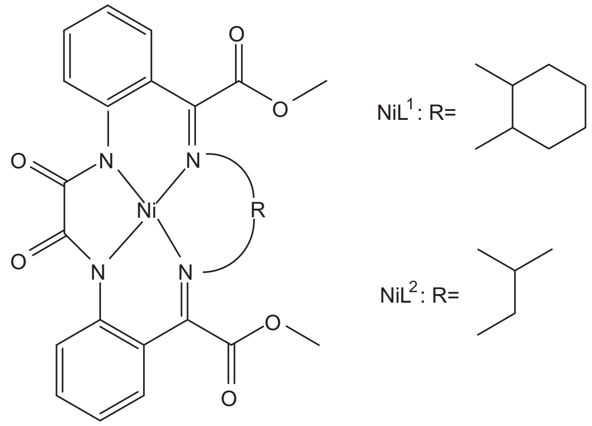

Scheme 1. NiL^1 and NiL^2.

also play a role in $\pi \cdots \pi$ interactions directing molecular recognition and packing in crystals [19].

2. Experimental

All starting chemicals were of reagent grade and used as purchased. The macrocyclic complex ligands NiL^1 and NiL^2 were prepared as described [16, 18]. Elemental analyses were performed on a Perkin-Elmer 240 analyzer. The IR spectra were recorded as KBr pellets on a BIO-RAD 3000 infrared spectrophotometer from 4000 to 400 cm^{-1}.

2.1. *Synthesis of* $[Co(NiL^1)_2(SCN)_2]$ *(1)*

The mixture of 0.1368 g (0.25 mmol) NiL^1, 0.110 g (0.30 mmol) $Co(ClO_4)_2 \cdot 6H_2O$, 0.0367 g (0.38 mmol) KSCN, and 25 mL CH_3OH was stirred at 62°C for 30 min. After cooling to room temperature, the mixture was filtered. The filtrate was then stored at room temperature for 25 days and red-violet crystals suitable for X-ray single-crystal analysis were obtained. Yield: 55.4%. Anal. Calcd for $C_{54}H_{48}CoN_{10}Ni_2O_{12}S_2$ (%): C, 51.04; H, 3.78; N, 11.03. Found(%): C, 50.97; H, 3.84; N, 11.05. FT-IR (KBr, cm^{-1}): 2069(s), 1737(s), 1602(s), 1585(s), 1554(s), 1441(s), 1345(s), 1206(s).

2.2. *Synthesis of* $[Co(NiL^2)_2(H_2O)_2](ClO_4)_2 \cdot 2C_2H_5OH$ *(2)*

The mixture of 0.1014 g (0.20 mmol) NiL^2, 0.0732 g (0.20 mmol) $Co(ClO_4)_2 \cdot 6H_2O$, and 35 mL C_2H_5OH was stirred at 65°C for 10 min. After cooling to room temperature, the mixture was filtered. The filtrate was then stored at room temperature for 24 days and orange crystals suitable for X-ray single-crystal analysis were obtained. Yield: 66.9%. Anal. Calcd for $C_{50}H_{56}Cl_2CoN_8Ni_2O_{24}$ (%): C, 42.86; H, 4.03; N, 8.00%. Found (%):

C, 43.10; H, 3.87; N, 8.25. FT-IR (KBr, cm^{-1}): 1730(s), 1600(s), 1580(s), 1553(s), 1442(s), 1341(s), 1209(s), 1100(s).

2.3. *X-ray structure determinations*

Diffraction data for **1** and **2** were collected on a Bruker Smart-1000-CCD area detector with Mo-Kα radiation ($\lambda = 0.71073$ Å) and a graphite monochromator. Further details of crystal data, data collection, and refinement are listed in table 1. The structures were solved by direct methods and subsequent Fourier difference techniques (SHELXS-97) and refined using full-matrix least-squares on F^2 with anisotropic thermal parameters for all non-hydrogen atoms (SHELXL-97) [20]. Hydrogens were added geometrically and refined with riding model position parameters and fixed isotropic thermal parameters. Selected bond lengths and angles are given in table 2 for **1** and table 3 for **2**.

3. Results and discussion

3.1. *Syntheses*

Excess $Co(ClO)_2 \cdot 6H_2O$ was required for production of **1** and **2**. When NiL^i ($i = 1$ or 2) and $Co(ClO)_2 \cdot 6H_2O$ were in the theoretical molar ratio of 2 : 1, solid NiL^i rather than species containing both NiL^i and Co(II) were isolated. This method enables the formation of crystalline products [14].

3.2. *Crystal structures*

Compound **1** is a neutral centrosymmetric trinuclear complex (figure 1(top)), while **2** contains the centrosymmetric trinuclear complex dication $[Co(NiL^2)_2(H_2O)_2]^{2+}$ (figure 1 (bottom)), two perchlorates and two lattice ethanols. In the trinuclear entities of **1** and **2**, Co(II) and Ni(II) are linked by the oxamido groups from the macrocyclic ligands. All Ni's in the complexes have slightly distorted N_4 square-planar coordination. The deviations of the four nitrogen atoms and Ni from their mean planes are −0.055 to 0.079 Å in **1** and −0.047 to 0.020 Å in **2**. Two phenyl rings of each complex ligand tilt slightly toward the same side of the NiN_4 plane with dihedral angles between the NiN_4 plane and two phenyl rings 12.7° and 26.6° in **1**, and 8.7° and 17.1° in **2**. The oxamido group tilts toward the other side of the NiN_4 plane, with a dihedral angle of 27.5° in **1** and 25.0° in **2**. All the Ni–N bonds are very short (1.859–1.902 Å in **1** and 1.850–1.876 Å in **2**, tables 2 and 3), which implies that the coordinating capabilities of the deprotonated oxamido and imino nitrogen atoms are very strong. The Co(II) in **1** takes a distorted octahedral coordination geometry with four oxygen atoms from two oxamido groups of two NiL^1 ligands in the equatorial positions and two NCS^- in the axial positions. Co(II) in **2** has a distorted octahedral coordination environment with four oxygen atoms from two oxamido groups of two NiL^2 ligands in equatorial positions and two water molecules in axial positions. In each trinuclear entity, the Ni and Co form a linear arrangement with a Ni···Co distance of 5.303 Å for **1** and 5.248 Å for **2**.

Table 1. Crystal data and structure refinements for **1** and **2**.

Compound	**1**	**2**
Formula	$C_{54}H_{48}CoN_{10}Ni_2O_{12}S_2$	$C_{50}H_{56}Cl_2CoN_8Ni_2O_{24}$
Formula weight	1269.49	1400.28
Color and habit	Red-violet, block	Orange, block
Temperature (K)	294(2)	293(2)
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$	$P2_1/n$
Unit cell dimensions (Å, °)		
a	24.330(4)	13.859(3)
b	9.4792(15)	11.972(3)
c	26.230(4)	17.710(4)
β	116.885(2)	92.063(5)
Volume (Å^3), Z	5395.6(15), 4	2936.3(12), 4
Calculated density (g cm^{-3})	1.563	1.584
Absorption coefficient (mm^{-1})	1.145	1.093
$F(000)$	2612	1442
Crystal size (mm^3)	0.28 × 0.18 × 0.12	0.25 × 0.15 × 0.10
θ range for data collection (°)	1.74–26.36	1.83–25.02
h, k, l ranges	−29 to 30, −10 to 11, −32 to 24	−16 to 11, −13 to 14, −17 to 21
Reflections collected	14,698	11,992
Unique reflections	5495 ($R_{int} = 0.0365$)	5184 ($R_{int} = 0.0974$)
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Refinement methods	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	5495/0/369	5184/217/469
Goodness-of-fit on F^2	1.037	0.964
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0438$, $wR_2 = 0.1047$	$R_1 = 0.0686$, $wR_2 = 0.1254$
R indices (all data)	$R_1 = 0.0768$, $wR_2 = 0.1244$	$R_1 = 0.1637$, $wR_2 = 0.1556$
Largest difference peak and hole (e Å^{-3})	1.085 and −0.543	0.636 and −0.339

Table 2. Selected bond lengths (Å) and angles (°) for **1**.

Co(1)–O(1)	2.155(2)	N(2)–C(2)	1.332(4)
Co(1)–O(2)	2.162(2)	N(3)–C(9)	1.288(4)
Co(1)–N(5)	2.054(4)	N(3)–C(12)	1.480(4)
Ni(1)–N(1)	1.859(3)	N(4)–C(17)	1.514(4)
Ni(1)–N(2)	1.878(3)	N(4)–C(18)	1.299(4)
Ni(1)–N(3)	1.860(3)	C(1)–O(1)	1.237(4)
Ni(1)–N(4)	1.902(3)	C(2)–O(2)	1.247(4)
N(1)–C(1)	1.350(4)	C(1)–C(2)	1.519(5)
N(1)–Ni(1)–N(3)	171.55(13)	C(26)–N(1)–Ni(1)	127.9(2)
N(1)–Ni(1)–N(4)	94.37(12)	C(2)–N(2)–C(3)	122.9(3)
N(2)–Ni(1)–N(3)	92.26(12)	C(2)–N(2)–Ni(1)	111.8(2)
N(3)–Ni(1)–N(4)	87.33(12)	C(3)–N(2)–Ni(1)	125.3(2)
N(4)–Ni(1)–N(2)	179.53(13)	C(9)–N(3)–C(12)	121.5(3)
O(1)–Co(1)–O(2)	77.59(9)	C(9)–N(3)–Ni(1)	128.2(2)
O(1)–Co(1)–O(1)^i	180.0	C(12)–N(3)–Ni(1)	108.9(2)
O(1)–Co(1)–O(2)^i	102.41(9)	C(18)–N(4)–C(17)	122.5(3)
O(2)–Co(1)–O(2)^i	180.0	C(18)–N(4)–Ni(1)	125.4(2)
C(1)–N(1)–Ni(1)	109.9(2)	C(17)–N(4)–Ni(1)	111.6(2)
C(1)–N(1)–C(26)	121.8(3)		

Symmetry code ^{i}: $-x+1/2$, $-y+1/2$, $-z$.

The N(1)–C(1) and N(2)–C(2) bonds in the oxamido groups of **1** and **2** have lengths of 1.324–1.350 Å, which are longer than the N=C double bonds (N(3)–C(9) and N(4)–C(18) in **1** and N(3)–C(9) and N(4)–C(15) in **2** (1.285–1.299 Å)), but significantly shorter than the N–C single bonds (N(3)–C(12) and N(4)–C(17) in **1** and N(3)–C(12)

Table 3. Selected bond lengths (Å) and angles (°) for **2**.

Co(1)–O(1)	2.088(4)	N(2)–C(2)	1.335(7)
Co(1)–O(2)	2.140(4)	N(3)–C(9)	1.285(8)
Co(1)–O(3)	2.068(4)	N(3)–C(12)	1.504(14)
Ni(1)–N(1)	1.876(5)	N(4)–C(14)	1.554(12)
Ni(1)–N(2)	1.866(5)	N(4)–C(15)	1.287(8)
Ni(1)–N(3)	1.866(5)	C(1)–O(1)	1.249(7)
Ni(1)–N(4)	1.850(6)	C(2)–O(2)	1.251(7)
N(1)–C(1)	1.324(7)	C(1)–C(2)	1.516(8)
O(1)–Co(1)–O(2)	77.53(15)	N(4)–Ni(1)–N(3)	86.1(3)
O(2)–Co(1)–O(3)	90.09(18)	C(1)–N(1)–C(23)	122.0(5)
O(3)–Co(1)–O(1)	90.1(2)	C(1)–N(1)–Ni(1)	109.9(4)
O(1)–Co(1)–O(1)$^{\mathrm{i}}$	180.0(1)	C(23)–N(1)–Ni(1)	127.1(4)
O(1)–Co(1)–O(2)$^{\mathrm{i}}$	102.47(16)	C(2)–N(2)–C(3)	121.6(5)
O(2)–Co(1)–O(2)$^{\mathrm{i}}$	180.0(1)	C(2)–N(2)–Ni(1)	110.4(4)
O(3)–Co(1)–O(1)$^{\mathrm{i}}$	89.9(2)	C(3)–N(2)–Ni(1)	127.7(4)
O(3)–Co(1)–O(2)$^{\mathrm{i}}$	89.91(18)	C(9)–N(3)–C(12)	120.6(8)
O(3)–Co(1)–O(3)$^{\mathrm{i}}$	180.0(2)	C(9)–N(3)–Ni(1)	128.5(5)
N(2)–Ni(1)–N(1)	86.7(2)	C(12)–N(3)–Ni(1)	110.2(7)
N(2)–Ni(1)–N(3)	92.9(2)	C(14)–N(4)–Ni(1)	112.6(7)
N(3)–Ni(1)–N(1)	175.9(2)	C(15)–N(4)–C(14)	115.9(7)
N(4)–Ni(1)–N(1)	94.0(2)	C(15)–N(4)–Ni(1)	128.3(5)
N(4)–Ni(1)–N(2)	176.7(2)		

Symmetry code $^{\mathrm{i}}$: $-x+1$, $-y+1$, $-z+2$.

and N(4)–C(14) in **2** (1.480–1.554 Å)). The sum of the three bond angles around each amidate nitrogen is close to 360° (356.8–360.0°). Thus the amidate nitrogen atoms are sp^2-hybridized and the π-electrons on these atoms and the carbonyls are delocalized. The C–C bonds in the oxamido groups have lengths of single bonds (C(1)–C(2) = 1.519(5) Å in **1** and 1.516(8) Å in **2**). The above analyses suggest that each oxamido is divided into two π-systems, each of which includes a carbonyl and an amidate nitrogen. The Schiff base groups are not involved in conjugated systems, evidenced by the normal lengths of the C–C and C–N single bonds around C=N.

Each of the two NiL$^{\mathrm{i}}$ fragments of every trinuclear entity of **1** and **2** overlaps with NiL$^{\mathrm{i}}$ fragments of neighboring trinuclear entities (figures S1 and S2) with close distances. Many of the distances (tables 4 and 5) between the overlapping NiL$^{\mathrm{i}}$ fragments fall into the range of $\pi\cdots\pi$ interactions (<3.80 Å) [19, 21]. Therefore, rich $\pi\cdots\pi$ interactions link the trinuclear entities to form 2-D layers in **1** and **2** (figures S1 and S2). The usually reported $\pi\cdots\pi$ interactions are those between aromatic π-systems. However, non-aromatic π-systems can also be involved in $\pi\cdots\pi$ interactions [19, 21]. N(3) and C(9) in **1** and N(2), N(3), Ni(1), and C(9) in **2**, which are involved in $\pi\cdots\pi$ interactions (tables 4 and 5), belong to non-aromatic π-systems. NiL$^{\mathrm{i}}$ type fragments can stack *via* $\pi\cdots\pi$ interactions in diverse arrangements as shown in figures S1 and S2 and tables 4 and 5 and the literature [12–14, 16, 17, 19].

3.3. *IR spectroscopic properties*

Bands at 1737 and 1730 cm^{-1} in the IR spectra of **1** and **2**, respectively, are absorptions of C=O (ester) [12–16]. Bands at 1602 cm^{-1} for **1** and 1600 cm^{-1} for **2** can be assigned to the absorptions of the oxamido C=O coordinated to Co^{2+}. Bands at 1585 cm^{-1} for **1**

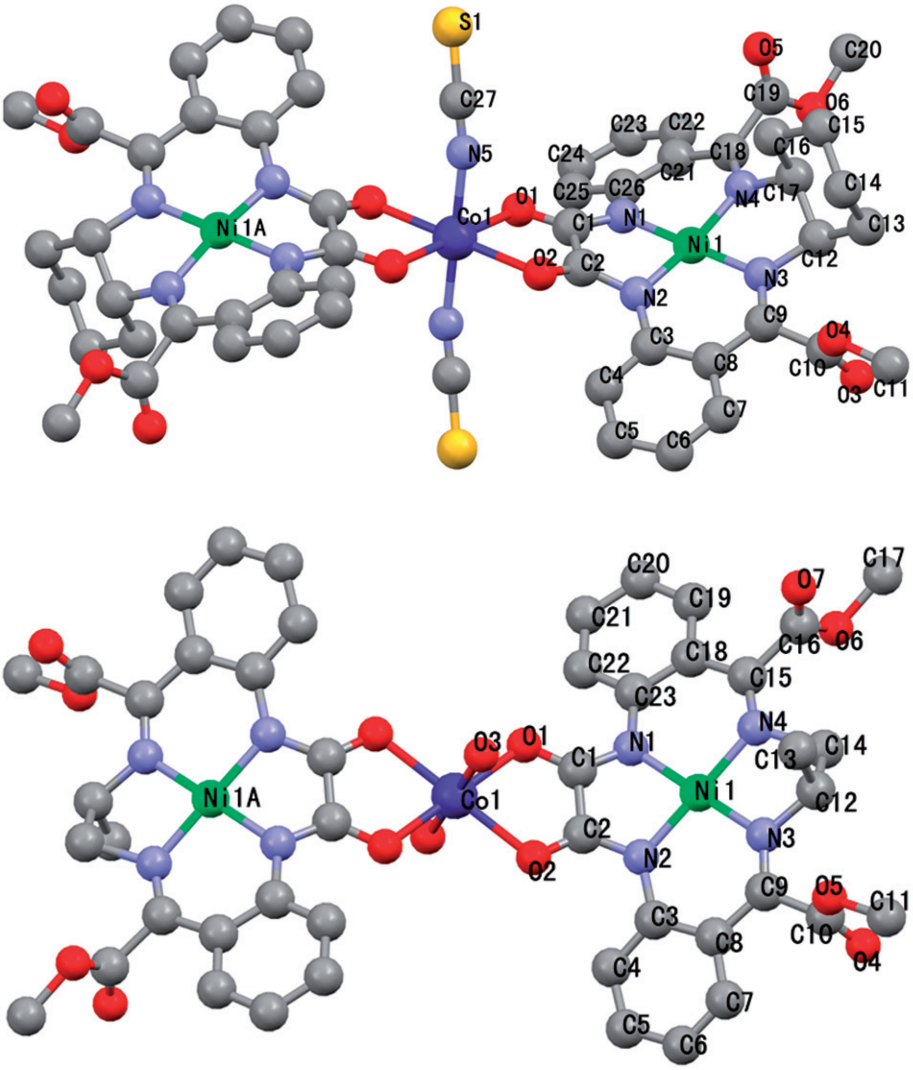

Figure 1. Structures of $[Co(NiL^1)_2(NCS)_2]$ in **1** (top) and $[Co(NiL^2)_2(H_2O)_2]^{2+}$ in **2** (bottom).

Table 4. Contact distances (Å) between neighboring trinuclear molecules of **1**.

$N(3)\cdots C(23)^i$	3.745(5)	$C(23)\cdots C(8)^i$	3.339(6)
$C(3)\cdots C(22)^i$	3.569(6)	$C(23)\cdots C(9)^i$	3.460(6)
$C(7)\cdots C(23)^i$	3.435(6)	$C(21)\cdots C(23)^j$	3.569(6)
$C(8)\cdots C(22)^i$	3.488(6)	$C(22)\cdots C(23)^j$	3.692(5)
$C(8)\cdots C(23)^i$	3.339(6)	$C(22)\cdots C(24)^j$	3.725(6)
$C(9)\cdots C(23)^i$	3.460(6)	$C(23)\cdots C(21)^j$	3.569(6)
$C(22)\cdots C(3)^i$	3.569(6)	$C(23)\cdots C(22)^j$	3.692(5)
$C(22)\cdots C(8)^i$	3.488(6)	$C(23)\cdots C(26)^j$	3.768(6)
$C(23)\cdots N(3)^i$	3.745(5)	$C(24)\cdots C(22)^j$	3.725(6)
$C(23)\cdots C(7)^i$	3.435(6)	$C(26)\cdots C(23)^j$	3.768(6)

Symmetry code ^{i}: $-x, -y, -z$; ^{j}: $-x, 1-y, -z$.

Table 5. Contact distances (Å) between neighboring trinuclear cations of **2**.

Ni(1)···C(20)^{i}	3.732(8)	C(20)···N(3)^{j}	3.707(9)
Ni(1)···C(21)^{i}	3.357(7)	C(20)···C(3)^{j}	3.442(9)
N(2)···C(20)^{i}	3.648(9)	C(20)···C(8)^{j}	3.471(9)
N(3)···C(20)^{i}	3.707(9)	C(20)···C(9)^{j}	3.681(5)
N(3)···C(21)^{i}	3.539(9)	C(21)···Ni(1)^{j}	3.357(7)
C(3)···C(20)^{i}	3.442(9)	C(21)···N(3)^{j}	3.539(9)
C(7)···C(19)^{i}	3.754(6)	C(3)···C(6)^{k}	3.798(9)
C(8)···C(19)^{i}	3.572(9)	C(3)···C(7)^{k}	3.527(9)
C(8)···C(20)^{i}	3.471(9)	C(5)···C(9)^{k}	3.745(1)
C(9)···C(19)^{i}	3.779(4)	C(6)···C(3)^{k}	3.798(9)
C(9)···C(20)^{i}	3.681(5)	C(6)···C(8)^{k}	3.733(9)
C(19)···C(7)^{j}	3.754(6)	C(7)···C(3)^{k}	3.527(9)
C(19)···C(8)^{j}	3.572(9)	C(7)···C(8)^{k}	3.721(9)
C(19)···C(9)^{j}	3.779(4)	C(8)···C(6)^{k}	3.733(9)
C(20)···Ni(1)^{j}	3.732(8)	C(8)···C(7)^{k}	3.721(9)
C(20)···N(2)^{j}	3.648(9)	C(9)···C(5)^{k}	3.745(1)

Symmetry code ^{i}: $3/2-x$, $1/2+y$, $3/2-z$; ^{j}: $3/2-x$, $-1/2+y$, $3/2-z$; ^{k}: $-x+1$, $-y$, $-z+2$.

and 1580 cm^{-1} for **2** are attributed to ν(C=N). The band at 2069 cm^{-1} in **1** originates from SCN^{-}. The broad band at 1100 cm^{-1} in **2** corresponds to ClO_4^-.

4. Conclusion

Two new Ni^{II}Co^{II}Ni^{II} trinuclear complexes have been synthesized by using two macrocyclic oxamido complex ligands, which supports this type of complex ligands for linear trinuclear heterometalic complexes. Structural analyses indicate that all the Ni–N bonds are very short, implying strong coordination, and that the cavities of the macrocyclic ligands are perfectly fit in size for Ni(II). The NiL^{i} fragments can stack *via* $\pi\cdots\pi$ interactions in diverse arrays, and apart from the phenyl rings, non-aromatic π-systems including nitrogen atoms and the Ni(II) center are active in molecular stacking through $\pi\cdots\pi$ interactions.

Supplementary material

Supplementary online material available: figures S1 and S2. See DOI:______. Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 807839 for **1** and 807838 for **2**. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.uk or www: http://www.ccdc.cam. ac.uk).

Acknowledgments

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