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Hydrothermal syntheses, structures and properties of three cyclic tetranuclear complexes and one 1D chain complex with 3,5-dinitrosalicylate

De-Cai Wen^{a,b}, Shi-Xiong Liu^{a,*}, Joan Ribas^c

^a Department of Chemistry, Fuzhou University, Fuzhou 350002, PR China ^b Department of Chemistry, Longyan University, Longyan 364000, PR China ^c Departament de Química Inorgànica, Universitat de Barcelona, Diagonal, 647, 08028 Barcelona, Spain

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Abstract

The hydrothermal reactions of $Co(OAc)_2 \cdot 4H_2O$, 3,5-dinitrosalicylate $(3,5-(NO_2)_2sal)$ and 2,2'-bipyridine (2,2'-bipy) with different reaction periods give metallamacrocycles 1 and 2 with the same chemical formula $Co_4(2,2'-bipy)_4\{3,5-(NO_2)_2sal\}_4$. Replacing $Co-(OAc)_2 \cdot 4H_2O$ with $Zn(NO_3)_2 \cdot 6H_2O$, using the same synthetic procedures, results in the formation of compound $[Zn(2,2'-bipy)_{\{3,5-(NO_2)_2sal\}}_n]$, (3) with a 1D chain structure and the metallamacrocycle compound $Zn_4(2,2'-bipy)_4\{3,5-(NO_2)_2sal\}_4$ (4). Compounds 1 and 2 crystallize as two different polymorphs of cyclic tetranuclear compounds. Compounds 3 and 4 are polymorphic too. The compounds 1 and 4 are isomorphous. The weak coordination interactions have significant influence on the spacial orientations of the 3,5-(NO_2)_2sal ligand, and may affect the crystallization processes. There are antiferromagnetic interactions in the cyclic tetranuclear cobalt(II) compounds 1 and 2. Compound 3 exhibits weak fluorescent emission in the solid state at room temperature. © 2007 Elsevier Ltd. All rights reserved.

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1. Introduction

Self-assembly in metallamacrocycles is a growing area at the forefront of modern supramolecular chemistry. Many diverse metallamacrocycles, such as molecular triangles, squares, rectangles, pentagons and hexagons, have been synthesized [1,2]. Pd(II) and Pt(II) units and N-donor ligands are the most favorite building blocks, and these species are highly charged. Except for 4,4'-bipy derivatives and imidazolate derivatives, most of the ligands used in the formation of metallamacrocycles are easily broken during hydrothermal reactions. Therefore, most of the syntheses of metallamacrocycles are solution reactions. Formation of metallamacrocycles by hydrothermal reactions is quite rare. On the other hand, considerable research effort has

* Corresponding author. Tel./fax: +86 591 83729860.

E-mail address: shixiongliu@yahoo.com (S.-X. Liu).

been focused on the study of polymorphs and isomorphous compounds in supramolecular chemistry [3,4].

Many carboxylate ligands have been shown to be good building blocks in the preparation of polynuclear complexes with desired topologies owing to their rich coordination modes [5]. Although a lot of carboxylate complexes have been studied, reports on the syntheses and magnetic properties of pentacoordinated cobalt(II) carboxylate complexes are far less in number.

We found that the choice of ligand plays an important role in preparing new metallamacrocycles. The self-assembly of decanuclear metallacrowns based on 3d-series metals M(III) with *N*-acyl salicylhydrazides was reported in our group [6a]. As shown in Scheme 1, the fully deprotonated salicylate(sal²⁻) can act in two coordination modes: monochelating-bridging (Ia) and bichelating (Ib). Acting as mode Ib, sal²⁻ may be a good linker to generate neutral metallamacrocycles with M(II), sal²⁻ in this case is similar

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Scheme 1. Binding models of sal²⁻ in complexes 1-4 and binding mode of shi³⁻ and xshz³⁻ ligands.



Scheme 2. Formation pathways of complexes 1-4.

to $xshz^{3-}$ (*N*-substituted salicylhydrazidate, H₃xshz) or shi^{3-} (substituted salicylhydroxamic acid, H₃shi) [1a,6,7]. There is a weak coordination between M2 and O2 in model *Ib*. The alternation between the existence and the non-existence of weak coordination may lead to polymorphs.

As a continuation of our effort in the formation of metallamacrocycles, we attempted to explore the assembly of metallamacrocycles by hydrothermal reactions, using 3d-series metals M(II), 3,5-dinitrosalicylate (3,5-(NO₂)₂sal) and 2,2'-bipyridine (2,2'-bipy). Herein, we report the syntheses, crystal structures and properties of four Co/Zn $3,5-(NO_2)$ sal complexes. Among the four title compounds, the cyclic tetranuclear cobalt compounds 1 and 2 are polymorphic, and the zinc compounds 3 and 4 are polymorphic too. Complex 3 has a 1D chain structure while the complex 4 has a cyclic tetranuclear structure. Compounds 1 and 4 form an isomorphous pair. The title complexes 1, 2 and 4 are the first examples of a 3,5-(NO₂)₂sal complex with a metallamacrocyclic structure. The formation pathway of the title compounds 1-4 is shown in Scheme 2. This research represents an interesting fact that different isomeric complexes can be obtained by a simple change of the reaction time.

2. Experimental

2.1. Materials and general procedures

All of the chemicals were obtained from commercial sources and were used without further purification. Ele-

mental analyses were conducted on a Perkin-Elmer 2400 CHN elemental analyzer. Magnetic measurements were carried out in the "Servei de Magnetoquímica (Universitat de Barcelona)" on polycrystalline samples (30 mg) with a Quantum Design SQUID MPMS-XL magnetometer working in the 2–300 K range. The magnetic field was 0.1 T. The diamagnetic corrections were evaluated from Pascal's constants. Fluorescence spectroscopy was performed on a Perkin-Elmer LS 55 luminescence spectrometer.

2.2. Synthesis of complexes

2.2.1. Synthesis of $Co_4(2,2'-bipy)_4\{3,5-(NO_2)_2sal\}_4(1)$

A mixture of $Co(OAc)_2 \cdot 4H_2O(0.1 \text{ mmol})$, 2,2'-bipy (0.1 mmol), 3,5-dinitrosalicylic acid (0.2 mmol) and distilled water (10 ml), with the pH value adjusted to 7 by addition of 1 M NaOH solution, was put into a Teflonlined autoclave (20 mL) and then heated at 180 °C for 48 h. Deep brown block-like crystals of 1 in 93% yield based on Co were obtained. *Anal.* Calc. for C₆₈H₄₀N₁₆-O₂₈Co₄: C, 46.27; H, 2.2; N, 12.70. Found: C, 46.22; H, 2.25; N, 12.75%.

2.2.2. Synthesis of $Co_4(2,2'-bipy)_4\{3,5-(NO_2)_2sal\}_4$ (2)

The same mixture as that for **1** was used, with the reaction at 180 °C for 72 h, resulting in deep brown block-like crystal of **2** in 92% yield based on Co. *Anal.* Calc. for $C_{68}H_{40}N_{16}O_{28}Co_{4}$: C, 46.27; H, 2.2; N, 12.70. Found: C, 46.19; H, 2.23; N, 12.76%.

2.2.3. Synthesis of $[Zn(2,2'-bipy) \{3,5-(NO_2)_2 sal\}]_n$ (3)

The same synthetic procedure as that for **1** was used except that $Co(OAc)_2 \cdot 4H_2O$ was replaced by $Zn(NO_3)_2 \cdot 6H_2O$, giving yellow block-like crystals of **3** in 92% yield based on Zn. *Anal.* Calc. for $C_{17}H_{10}N_4O_7Zn$: C, 45.61; H, 2.25; N, 12.52. Found: C, 45.55; H, 2.30; N, 12.54%.

2.2.4. Synthesis of $Zn_4(2,2'-bipy)_4\{3,5-(NO_2)_2sal\}_4$ (4)

The same mixture as that for **3** was used, with the reaction at 180 °C for 72 h, resulting in **3** in about 70% yield and light yellow block-like crystals of **4** in about 15% yield based on Zn. *Anal.* Calc. for $C_{68}H_{40}N_{16}O_{28}Zn_4$: C, 45.61; H, 2.25; N, 12.52. Found: C, 45.52; H, 2.26; N, 12.48%.

2.3. X-ray crystallography

X-ray diffraction measurements were carried out at 293 K with graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å) on a Bruker SMART CCD 1000 diffractometer for **2** and on a Rigaku R-AXIS RAPID Weissengberg IP diffractometer for **1**, **3** and **4**. The structures were solved by direct methods (SHELXTL-97) and refined on F^2 by full-matrix least-squares techniques. The high values of the thermal parameters of the oxygen atoms of the NO₂ groups in complexes **1**, **2** and **4** suggest disordered positions of these oxygen atoms. Therefore, these oxygen

Table 1 Crystallographic data for complexes 1–4

atoms are in disordered positions and were refined isotropically. The crystallographic data for 1–4 are summarized in Table 1.

3. Results and discussion

3.1. Structural description

As illustrated in Fig. 1, the centrosymmetrical molecular square structure of 1 is built up of four cobalt(II) cations (Co1, Co2, Co1A and Co2A, symmetry code A, -x + 1, -y, -z + 1), four bridging 3,5-(NO₂)₂sal ligands and four 2,2'-bipy ligands. Selected bond lengths and angles are listed in Table 2.

Each Co^{II} ion is pentacoordinated by three oxygen atoms from two 3,5-(NO₂)₂sal ligands and two nitrogen atoms from a 2,2'-bipy ligand. The Co1 atom has a distorted square-pyramidal geometry with a τ value of 0.03 [8]. However, the coordination sphere of Co2 is between square-pyramidal and the trigonal bipyramidal, with a τ value of 0.40. When the Co1–O9 and Co2–O2A distances (2.504(1) Å and 2.705(4) Å) are considered as weak coordination, the Co1 and Co2 centers may be regarded as having distorted octahedral conformations.

Every one of the four $3,5-(NO_2)_2$ sal ligands exhibits a bichelating coordination mode (Scheme 1(Ib)). Therefore, neighboring cobalt atoms are connected by one 3,5-

Compound	1	2	3	4
Formula	C ₆₈ H ₄₀ N ₁₆ O ₂₈ Co ₄	C ₆₈ H ₄₀ N ₁₆ O ₂₈ Co ₄	$C_{17}H_{10}N_4O_7Zn$	C68H40N16O28Zn4
Formula weight	1764.88	1764.88	447.66	1790.64
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a (Å)	13.015(3)	14.715(2)	12.411(5)	12.2799(1)
b (Å)	12.842(3)	21.907(3)	16.008(5)	13.5024(3)
<i>c</i> (Å)	21.541(6)	21.593(3)	8.721(3)	22.1376(6)
α (°)	90	90	90	90
β (°)	103.235(9)	94.865(2)	93.84(2)	102.282(2)
γ (°)	90	90	90	90
$V(\text{\AA}^3)$	3505(2)	6936(1)	1729.8(1)	3586.6(1)
Z	2	4	4	2
$D_{\rm calc} ({\rm g/cm^{-3}})$	1.672	1.690	1.473	1.658
<i>T</i> (K)	293(2)	293(2)	293(2)	293(2)
$\mu (\mathrm{mm}^{-1})$	1.031	1.042	1.473	1.420
<i>F</i> (000)	1784	3568	904	1808
$\theta_{\min, mum}, \theta_{\max, mum}(^{\circ})$	3.17, 27.47	1.86, 25.00	3.03, 27.47	1.70, 27.48
h _{minimum-maximum}	$-15 \rightarrow 16$	$-17 \rightarrow 17$	$-16 \rightarrow 16$	$0 \rightarrow 15$
k _{minimum-maximum}	$-16 \rightarrow 16$	$-26 \rightarrow 25$	-20 ightarrow 20	$0 \rightarrow 17$
l _{minimum-maximum}	$-27 \rightarrow 27$	$-24 \rightarrow 25$	$-10 \rightarrow 11$	-28 ightarrow 28
R _{int}	0.0359	0.0538	0.0235	0.0538
Number of unique data	7979	11 595	3954	8200
Number of observed	5784	6468	3448	4145
Number of variables	517	1041	262	515
$R_1 [I > 2\sigma(I)]$	0.0550	0.0439	0.0258	0.0565
$wR_2 [I \ge 2\sigma(I)]$	0.1516	0.1054	0.0666	0.1441
Goodness-of-fit	1.063	0.944	1.032	0.949
$(\Delta p)_{\text{maximum,minimum}} (e/Å^3)$	0.792 (-0.638)	0.690 (-0.432)	0.316 (-0.238)	0.674 (-0.570)
$(\Delta/\sigma)_{\text{maximum}}, (\Delta/\sigma)_{\text{minimum}}$	0.001, 0.000	0.001, 0.000	0.000, 0.000	0.001, 0.000



Fig. 1. Molecular structure of complex 1 with 30% probability ellipsoids, hydrogen atoms are omitted for clarity. Symmetry code A, -x + 1, -y, -z + 1. Only one orientation of the disordered NO₂ groups is presented.

Table 2 Selected bond lengths (Å) and angles (°) for complexes 1 and 4^{a}

Complex 1		Complex 4	
Co(1)–O(2)	2.026(3)	Zn(1)–O(2)	2.041(3)
Co(1)–O(3)	1.995(3)	Zn(1) - O(3)	1.979(3)
Co(1)–O(8)	2.078(3)	Zn(1)–O(8)	2.003(3)
Co(1)-N(3)	2.115(3)	Zn(1)-N(4)	2.154(4)
Co(1)-N(4)	2.116(3)	Zn(1)-N(3)	2.095(4)
Co(2)–O(9)	2.027(2)	Zn(2)-O(9)	2.013(3)
Co(2)–O(10)	1.978(3)	Zn(2)–O(10)	2.016(4)
Co(2)-O(1A)	2.010(3)	Zn(2)-O(1A)	2.025(4)
Co(2)-N(7)	2.108(3)	Zn(2)-N(7)	2.153(5)
Co(2)–N(8)	2.064(3)	Zn(2)–N(8)	2.072(4)
O(3)–Co(1)–O(2)	90.6(1)	O(3)–Zn(1)–O(2)	90.1(1)
O(3)-Co(1)-O(8)	96.2(1)	O(3) - Zn(1) - O(8)	105.9(2)
O(2)–Co(1)–O(8)	91.4(1)	O(2) - Zn(1) - O(8)	95.2(1)
O(3)-Co(1)-N(3)	97.5(1)	O(3) - Zn(1) - N(3)	112.6(2)
O(2)-Co(1)-N(3)	92.2(1)	O(2) - Zn(1) - N(3)	92.2(2)
O(8)-Co(1)-N(3)	165.8(1)	O(8) - Zn(1) - N(3)	140.8(2)
O(3)-Co(1)-N(4)	102.0(1)	O(3)-Zn(1)-N(4)	97.2(2)
O(2)-Co(1)-N(4)	164.0(1)	O(2)-Zn(1)-N(4)	169.0(2)
O(8)-Co(1)-N(4)	97.0(1)	O(8)-Zn(1)-N(4)	90.8(2)
N(3)-Co(1)-N(4)	76.5(1)	N(3)-Zn(1)-N(4)	77.4(2)
O(9)-Co(2)-O(10)	88.5(1)	O(9)-Zn(2)-O(10)	87.8(1)
O(9)-Co(2)-O(1A)	151.4(1)	O(9)-Zn(2)-O(1A)	144.0(2)
O(10)-Co(2)-O(1A)	91.7(1)	O(10)-Zn(2)-O(1A)	90.9(2)
O(9)-Co(2)-N(7)	90.7(1)	O(9)-Zn(2)-N(7)	92.9(2)
O(10)-Co(2)-N(7)	175. 4(1)	O(10)-Zn(2)-N(7)	173.5(2)
O(1)A-Co(2)-N(7)	91.2(1)	O(1)A-Zn(2)-N(7)	92.3(2)
O(9)-Co(2)-N(8)	115.9(1)	O(9)-Zn(2)-N(8)	118.8(2)
O(10)-Co(2)-N(8)	98.5(1)	O(10)-Zn(2)-N(8)	96.5(2)
O(1)A-Co(2)-N(8)	92.4(1)	O(1)A-Zn(2)-N(8)	97.0(2)
N(7)-Co(2)-N(8)	77.8(1)	N(7)-Zn(2)-N(8)	77.6(2)

^a Symmetry code: A, -x + 1, -y, -z + 1.

 $(NO_2)_2$ sal ligand through the bridging oxygen atoms (O9, O2A, O9A and O2), generating a Co_4O_4 core of the molecular square. The four Co^{II} ions in the core are exactly coplanar. The Co...Co distances in the core are 4.319(2) and 4.617(9) Å along the side and 6.594(19) and 6.038(1) Å across the diagonal. The angles Co2–Co1–Co2A and Co1–Co2–Co1A in the core are 84.95(1)° and

95.05(1)°, respectively, indicating a slight deviations from an ideal square geometry.

Adjacent tetranuclear metallamacrocycles are further connected to each other by C–H...O hydrogen bonds [9] between the C–H group of the 2,2'-bipy ligand and the oxygen atom in the NO₂ groups of the 3,5-(NO₂)₂sal ligand, resulting in an extended 3D network structure (Fig. S1). The H...O distances are in the range of 2.43–2.53 Å. Detailed data are given in Table S1.

On comparison with the many substituted salicylhydroxamic acid and *N*-substituted salicylhydrazidate complexes, only a few $3,5-(NO_2)_2$ sal complexes have been found [10]. There are two types of structure for the known five $3,5-(NO_2)_2$ sal complexes, i.e. a 1D structure for $[Co^{II}(phen){3,5-(NO_2)_2sal^{2-}}]$ [10b] and [Mn(phen)- ${3,5-(NO_2)_2sal^{2-}}]$ [10c] and a discrete multinuclear structure for the other three complexes. To our knowledge, the title complexes **1**, **2** and **4** are the first examples of any $3,5-(NO_2)_2$ sal complex with a metallamacrocycle structure.

The molecular structure of complex 2 is shown in Fig. 2. Selected bond lengths and angles are listed in Table 3. The cyclic tetranuclear complex molecule $Co_4(2,2'-bipy)_4$ - $\{3,5-(NO_2)_2 \text{sal}\}_4$ (2) contains four cobalt(II) cations (Co1, Co2, Co3 and Co4), four 3,5-(NO₂)₂sal ligands and four 2,2'-bipy ligands. Two of the four 3,5-(NO₂)₂sal ligands bridge two neighboring $[Co(2,2'-bipy)]^{2+}$ corners through one bridging carboxylate oxygen atom (O2 or O16). For the other two 3,5-(NO₂)₂sal ligands, each one bridges two neighboring $[Co(2,2'-bipy)]^{2+}$ corners through two oxygen atoms (O8 and O9 or O22 and O23) in the carboxylate group. Therefore, four cobalt cations and four 3,5-(NO₂)₂sal ligands construct a molecular rhomboid structure with a $Co_4O_6C_2$ core. The molecular rhomboid structure in 2 is different from the molecular square structure in 1. The four neighboring Co...Co distances in the $Co_4O_6C_2$ core are 5.116(1), 4.247(1), 5.209(2) and 4.370(1) Å. The Co-Co-Co angles in the core are 101.10(1)°, 79.83(1)°, 101.35(1)° and 77.71(1)°.



Fig. 2. Molecular structure of complex **2** with 30% probability ellipsoids, hydrogen atoms are omitted for clarity. Only one orientation of the disordered NO₂ groups is presented.

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

	()8	e () - = =	
Co(1)-O(8)	1.968(3)	Co(3)-O(17)	1.971(3)
Co(1)–O(3)	1.970(3)	Co(3)–O(22)	1.986(3)
Co(1)–O(2)	2.036(3)	Co(3)-O(16)	2.024(3)
Co(1)-N(3)	2.056(3)	Co(3)–N(11)	2.067(3)
Co(1)-N(4)	2.127(3)	Co(3)–N(12)	2.107(3)
Co(2)-O(10)	1.975(3)	Co(4)–O(24)	1.974(3)
Co(2)–O(9)	2.001(3)	Co(4)–O(23)	1.995(3)
Co(2)-N(8)	2.092(3)	Co(4)–O(1)	2.061(3)
Co(2)-O(15)	2.098(3)	Co(4)-N(16)	2.087(3)
Co(2)-N(7)	2.114(3)	Co(4)-N(15)	2.103(3)
O(8)-Co(1)-O(3)	119.2(1)	O(10)-Co(2)-O(9)	88.8(1)
O(8)-Co(1)-O(2)	91.8(1)	O(10)-Co(2)-N(8)	93.9(1)
O(3)-Co(1)-O(2)	89.4(1)	O(9)-Co(2)-N(8)	110.5(1)
O(8)-Co(1)-N(3)	129.6(1)	O(10)-Co(2)-O(15)	102.4(1)
O(3)-Co(1)-N(3)	110.0(1)	O(9)-Co(2)-O(15)	146.5(1)
O(2)-Co(1)-N(3)	99.5(1)	N(8)-Co(2)-O(15)	100.3(1)
O(8)-Co(1)-N(4)	91.8(1)	O(10)-Co(2)-N(7)	167.0(1)
O(3)-Co(1)-N(4)	89.7(1)	O(9)-Co(2)-N(7)	86.3(1)
O(2)-Co(1)-N(4)	176.3(1)	N(8)-Co(2)-N(7)	76.6(1)
N(3)-Co(1)-N(4)	77.5(1)	O(15)-Co(2)-N(7)	88.2(1)
O(17)-Co(3)-O(22)	123.5(1)	O(24)-Co(4)-N(15)	168.3(1)
O(17)-Co(3)-O(16)	89.6(1)	O(23)-Co(4)-N(15)	86.8(1)
O(22)-Co(3)-O(16)	93.3(1)	O(1)-Co(4)-N(15)	89.3(1)
O(17)-Co(3)-N(11)	111.2(1)	N(16)-Co(4)-N(15)	77.4(1)
O(22)-Co(3)-N(11)	122.4(1)	O(24)-Co(4)-O(23)	89.8(1)
O(16)-Co(3)-N(11)	104.5(1)	O(24)-Co(4)-O(1)	100.0 (1)
O(17)-Co(3)-N(12)	87.1(1)	O(23)-Co(4)-O(1)	143.7(1)
O(22)-Co(3)-N(12)	87.9(1)	O(24)-Co(4)-N(16)	94.4(1)
O(16)-Co(3)-N(12)	176.7(1)	O(23)-Co(4)-N(16)	117.4(1)
N(11)-Co(3)-N(12)	77.4(1)	O(1)-Co(4)-N(16)	96.8(1)

There are two kinds of coordination modes for the four $3,5-(NO_2)_2$ sal ligands in complex **2**; the two of four ligands act in the monochelating-bridging mode (Scheme 1a), and the other two act in the bichelating mode (Scheme 1b), to give the $Co_4O_6C_2$ core of the molecular rhomboid.

The coordination geometry of two cobalt atoms, Co1 and Co3, is distorted trigonal bipyramidal, with τ values of 0.78 and 0.90, respectively. However, the coordination geometry of Co2 and Co4 can be described as a distorted octahedron because of the weak coordination (Co2–O16 = 2.431(3) Å, Co4–O2 = 2.518(3) Å).

There are some intermolecular C–H...O hydrogen bonds which form an extended 3D structure (Fig. S2). The H...O distances are in the range 2.396-2.523 Å (Table S1).

The 1D chain structure of complex **3** is given in Fig. 3. Selected bond lengths and angles are illustrated in

Table 4. Each Zn^{II} ion is pentacoordinated by three oxygen atoms of two 3,5-(NO₂)₂sal ligands and two nitrogen atoms of a 2,2'-bipy ligand. The coordination sphere is between square-pyramidal and trigonal bipyramidal, with a τ value of 0.32. Each 3,5-(NO₂)₂sal ligand adopts a monochelating-bridging mode (Scheme 1(Ia)) and links two Zn^{II} ions into a 1D chain structure along the *c* axis. The chain core is with a [-Zn-O-C-O-]_n repeat. The neighboring Zn1... Zn1A distance (Symmetry code: A *x*, -y + 1/2, z - 1/2) is 5.132(1) Å, and the Zn-Zn-Zn angle is 116.35(1)°. The 1D chains are further connected by C-H...O hydrogen bonds, resulting in a 3D supramolecular network structure (Fig. S3). The H...O distances are in the range 2.602– 2.670 Å (Table S1).

The zinc compound 4 and the cobalt compound 1 are isomorphous. The centrosymmetrical molecular square structure in 4 (Fig. S4) is the same as that in 1. Selected bond lengths and angles of complex 4 are listed in Table 2. In compound 4, each one of four bridging oxygen atoms (O2, O9, O2A and O9A, symmetry code A, -x + 1, -y, -z + 1) of the carboxylate groups from four 3,5-(NO₂)₂sal ligands bridges two zinc(II) cations to form an Zn₄O₄ core in the molecular square structure. The Zn. . .Zn distances in 4 are 4.746(4) and 4.663(2) Å along the side and 6.558(4) and 6.747(1) Å across the diagonal. The vertex angles for Zn2–Zn1–Zn2A and Zn1–Zn2–Zn1A are 91.63(1)° and 88.37(1)°, respectively. It indicates a quite ideal square geometry.

The coordination geometry for the four zinc(II) cations in **4** is between square-pyramidal and the trigonal bipyramidal, the τ values of the Zn1 and Zn2 polyhedra being 0.47 and 0.49, respectively. The Zn1–O9 distance is 2.881(4) Å, and the Zn2–O2A distance is 2.744(4) Å. When Zn1–O9 and Zn2–O2A are considered as weakly coordi-

Table 4							
Selected	bond	lengths	(Å) and	angles	(°)	for 3 ^a	L

U	()		
Zn(1)–O(1)A	1.983(1)	Zn(1)-N(4)	2.086(2)
Zn(1) - O(3)	1.994(1)	Zn(1)-N(3)	2.107(1)
Zn(1)–O(2)	2.019(1)	O(2)-Zn(1)-N(4)	91.29(5)
O(1)A1–Zn(1)–O(3)	93.72(6)	O(3)–Zn(1)–N(3)	92.16(5)
O(1)A1-Zn(1)-O(2)	93.92(5)	O(2)-Zn(1)-N(3)	163.17(5)
O(3) - Zn(1) - O(2)	88.87(5)	N(4)-Zn(1)-N(3)	78.03(5)
O(1)A-Zn(1)-N(4)	122.34(5)	O(1)A-Zn(1)-N(3)	102.77(5)
O(3) - Zn(1) - N(4)	143.82(5)		

^a Symmetry code: A, x, -y + 1/2, z - 1/2.



Fig. 3. 1D chain of complex **3** with 30% probability ellipsoids. Symmetry code A, $x_1 - y + 1/2$, z - 1/2.

nating, the coordination geometries of the Zn^{II} ions can be described as distorted octahedra. Each 3,5-(NO₂)₂sal ligand exhibits a bichelating coordination mode (Scheme 1 Ib).

The C-H...O hydrogen bonds in complex 4 (Table S1) bridge the adjacent tetranuclear metallamacrocycles to create an extended 3D network structure (Fig. S5).

3.2. Weak coordination interactions and coordination orientations

There exist weak coordination interactions M2...O2 between the O.O',O"-tridentate ligand 3,5-(NO₂)₂sal and the metal cation (Ib in Scheme 1) in compounds 1, 2 and 4. As shown in Table 5, the absolute value of the torsion angles O2-C-O1-M2 are between 0.2° and 8.7°, and the C-O1-M2 bridging angles are in the range 100.2-115.5°. When there are no weak coordination interactions of M2...O2 (Ia in Scheme 1), the torsion angles O2-C-O1-M2 in 2 and 3 are between 26.7° and 33.4° , and the C-O1-M2 bridging angles are in the range 125.6-128.1°. The strength of the weak coordination interactions among the four title compounds is of the following order: 1, 4 > 2 > 3. Coincidentally, compounds 1 and 4 have the molecular square structure, compound 2 has the molecular rhomboid structure while compound 3 has the chain structure. This suggests that the weak coordination interactions have significant influence on the space orientations of the 3,5-(NO₂)₂sal ligand, and may affect the crystallization processes and solid state architectures.

3.3. Magnetism

The temperature dependences of $\chi_M T$ (χ_M being the magnetic susceptibility for four Co^{II}ions) in complexes 1 and 2 are shown in Figs. 4 and 5 (from 300 K to 2 K), respectively. $\chi_M T$ at 300 K in 1 and 2 is close to 9 and 10.5 cm³ mol⁻¹ K, respectively, and these values are as expected for four isolated pentacoordinated Co^{II} ions. $\chi_M T$ in 1 monotonously decreases to reach 0.2 cm³

 mol^{-1} K at 2.00 K. $\chi_{\text{M}}T$ in **2** monotonously decreases to reach 1.0 cm³ mol⁻¹ K at 2.00 K. The shape of these curves for complexes 1 and 2 is characteristic of the occurrence of weak antiferromagnetic interactions between the Co^{II} centres. The antiferromagnetic behaviour in the two complexes is corroborated by plotting the reduced magnetization (M/ $N\beta$) versus H at 2 K. In both cases the shape of the curve is typical for an antiferromagnetic coupling, not very strong, and the values at 5 T are close to 4 N β instead of 12 (the theoretical values assuming g = 2.00 for four Co^{II} ions fully isolated). The pentacoordinated Co^{II} ion does not present spin-orbit coupling, such as occurs with the octahedral analogues. Thus, they can be treated as systems with S = 3/2 with the spin-hamiltonian formalism. Taking into account the tetranuclear character of 1 and 2 we have done the fit assuming two different J values (alternated) by means of the CLUMAG program [11]. The best fit is given by the exchange parameters $J_1 = -0.41 \text{ cm}^{-1}$, $J_2 = -0.33 \text{ cm}^{-1}$ and g = 2.21 for **1** and $J_1 = -0.36 \text{ cm}^{-1}$, $J_2 = -0.23 \text{ cm}^{-1}$ and g = 2.30 for **2**. The two set of values are similar, it being interesting to emphasize that for complex 1 the two J values are more similar, which agrees with



Fig. 4. Plot of $\chi_M T$ vs. *T* for complex 1. The solid line represents the best fit. Inset: plot of the reduced magnetization (M/N β) at 2 K.

Table 5

A comparison between weak coordination, torsion angles and bridging angles in complexes 1-4

1		· · · · ·	U			
Complex	M2 ^a	M2O2 distance (Å)	Weak coordination	O2–C–O1–M2 torsion angle (°)	C–O1–M2 bridging angle (°)	Structure type
1	Col	2.50(1)	yes	-0.2(4)	103.2(2)	molecular square
	Co2	2.705(4)	yes	8.7(4)	110.0(2)	_
2	Col	3.170(3)	no	26.7(5)	125.6(3)	molecular rhomboid
(Co2	2.431(3)	yes	4.8(4)	100.2(2)	
	Co3	3.251(3)	no	-31.7(5)	127.8(3)	
	Co4	2.518(3)	yes	-2.5(4)	103.2(3)	
3	Zn1	3.280(2)	no	-33.4(2)	128.1(1)	1D chain
4	Znl	2.881(4)	yes	8.7(6)	115.5(3)	molecular square
	Zn2	2.744(4)	yes	-1.6(6)	111.0(3)	ŕ

^a The symbols M2, O2, C, and O1 are the same as those in Scheme 1(Ib).



Fig. 5. Plot of $\chi_M T$ vs. *T* for complex **2**. The solid line represents the best fit. Inset: plot of the reduced magnetization (M/N β) at 2 K.

a structure that it is more square-like in **1** and more rhomboid-like in **2**. The small *J* values are due, in both cases, to the magnetic pathway created by the carboxylate bridging groups in a *syn-anti* configuration. The small overlap between the magnetic orbitals accounts for the weak coupling observed. This qualitative approach was already introduced by Kahn when studying this kind of *syn-anti* coordination mode [12].

3.4. Photoluminescence

The emission spectra of complex **3** and the free 3,5- $(NO_2)_2$ sal ligand in the solid state at room temperature have been investigated. Complex **3** exhibits blue fluorescent emission bands at ca. 485 nm upon excitation at ca. 360 nm (Fig. S6). These emissions are assigned to the intraligand fluorescent emission because similar emissions are observed for the free 3,5- $(NO_2)_2$ sal (Fig. S7) [13].

4. Conclusion

In summary, three cyclic tetranuclear complexes and one 1D chain structure complex have been prepared by the hydrothermal reactions of $Co(OAc)_2 \cdot 4H_2O/Zn(NO_3)_2 \cdot 6H_2O$, 3,5-(NO₂)₂sal and 2,2'-bipy with different reaction times. The cobalt complexes 1 and 2 constitute a pair of polymorphs. There is a molecular square structure with a Co_4O_4 core in 1 and a molecular rhomboid structure with a $Co_4O_6C_2$ core in 2. The zinc complexes 3 and 4 constitute a pair of polymorphs too. There is a 1D structure in 3 and a molecular square structure in 4. Our results demonstrate an interesting fact that polymorphic compounds with different structure types can be obtained by a simple change of the reaction time. Compounds 1 and 4 form an isomorphous pair.

The weak coordination interactions have a significant influence on the space orientations of the $3,5-(NO_2)_2$ sal ligand. There are antiferromagnetic interactions in the cyc-

lic tetranuclear pentacoordinated cobalt(II) complexes 1 and 2.

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Appendix A. Supplementary material

CCDC 617368, 617369, 617370 and 617371 contain the supplementary crystallographic data for **1**, **2**, **3** and **4**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2007.04.028.

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