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From Monomer Zinc–Oxamato Complexes to Tetranuclear Inverse 12-Membered and Octanuclear 12-Membered Metallacrowns

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Interaction of $ZnCl_2$ with Hpko (Hpko, di-2-pyridyl-ketonoxime) results in the formation of a uninuclear $Zn(Hpko)Cl_2$ (**1**) compound or in a 12-membered tetranuclear metallacrown $(OH)_2[inv12\text{-}MC_{Zn(II)N(pko)}\text{-}4]Cl_2$ (**2**) depending on the pH of the mother solution. The addition of H_3shi (H_3shi, salicylhydroxamic acid) leads to the formation of the octanuclear 12-membered tetranuclear metallacrown $[Zn_2]\{[Zn_2(pko)_4][12\text{-}MC_{Zn(II)N(shi)}\text{-}4](CH_3OH)_2\}$ (**3**). The metallacrown core of **2** is characterized as "inverse" because the zinc atoms, rather than oxygen atoms, are oriented toward the central cavity. Two triply bridging hydroxides are accommodated in the center of the metallacrown ring. The pko^- ligands form a propeller configuration that imposes absolute stereoisomerism with Λ and Δ chirality. Each hydroxo oxygen bridges two octahedral zinc atoms and a tetrahedral one. The octanuclear cluster $Zn_8(shi)_4(pko)_4(CH_3OH)_2$ contains a 12-membered tetranuclear metallacrown core constructed by four Zn metal atoms and four shi^{3-} ligands. So, a part of the cluster can be described as having the formally anionic $[12\text{-}MC_{Zn(II)N(shi)}\text{-}4]^{4-}$ core. Two of the zinc atoms are in octahedral coordination environment while for the other two the geometry is best described as distorted trigonal bipyramidal. The metallacrown core accommodates a binuclear compound with the formula $[Zn_2(pko)_4]$. Two of the ring metal ions create binuclear units with two zinc ions, respectively, with two oxamato oxygens, and two phenolato oxygens, of the four interlinked shi^{3-} ligands acting as bridging atoms.

Introduction

Metallomacrocycles have gained increasing attention over the past decade because of their potentially unique properties.[1–6] Metallacrowns are an example of this molecular class, which exhibits selective recognition of cations and anions, can display intramolecular magnetic exchange interactions, and can be used as building blocks for chiral layered solids[1]. While many types of molecular species can form complexes, their utility as hosts is quite limited unless there is a mechanism in place to allow the species to distinguish between different guests.[2–6] A number of different approaches can be used to induce changes in a potential host molecule that allow for differentiation of various guests. Among the changes in the host cavity are the size of the cavity, its shape, the number of coordination sites, and the type of coordinating species. The correlation between the size of a host cavity and its potential guest is a first criterion for selective molecular recognition. Because of the nature of the inorganic molecular recognition agents, not only is it possible that they could function as cation or anion recognition agents but also they may be able to selectively bind ionic compounds, recognizing the cation and the anion simultaneously.

Metallacrowns[7] exhibit a cyclic structure generally analogous to crown ethers[8–11] with transition metal ions and a nitrogen atom replacing the methylene carbons. The up to date reported metallacrowns have been prepared using hydroxamic acids and/or ketonoximic acids as constructing

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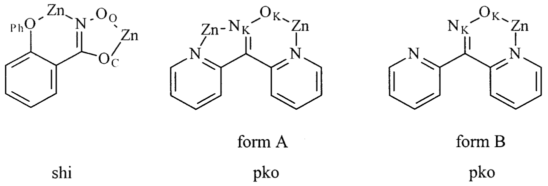
Scheme 1. Drawing Showing the Binding Modes of shi^{3-} and pko^{-} Ligands



ligands. Hpko is a bifunctional ligand that can bind metals in either five- or six-membered chelate rings (Scheme 1). The deprotonated di-2-pyridyl-ketonoxime can act in two binding modes: (i) bichelate and (ii) monochelate. In (i), the ketonoxime oxygen (O$_K$) and one pyridine nitrogen (N) bind to one metal atom and the other pyridine nitrogen (N); plus, the ketonoxime nitrogen (N$_K$) chelates an adjacent metal atom (form A). In (ii), only the ketonoxime oxygen (O$_K$) and one pyridine nitrogen (N) chelate to one metal atom (form B). The deprotonated salicylhydroxamic acid acts as a binucleating ligand with the carbonyl and oxamato oxygens (O$_C$ and O$_O$) binding to one metal and the phenolate oxygen (O$_{Ph}$), plus the oxamato nitrogen (N) chelating an adjacent metal atom. The juxtaposed five-membered and six-membered chelates form the basis of the metallacrown structure analogous to a 12-C-4 crown ether with the methylene carbons replaced with M and N.

These juxtaposed five- and six-membered chelate rings form the basis of the metallacrown ring through the [M−N−O−]$_n$ linkage. The cavity size of metallacrowns is well compared to organic crown ethers. [9-MC$_{M(ox)N(ligand)}$-3],[12−14] [12-MC$_{M(ox)N(ligand)}$-4],[15−22] and [15-MC$_{M(ox)N(ligand)}$-5][23−28] metallacrowns with cavity sizes of 0.35, 0.60, and 0.77 Å, respectively, and metal ions Mn^{III}, Fe^{III}, Ni^{II}, Cu^{II}, and V^{V}O, [12-MC-6],[29] [16-MC-8],[30] [18-MC-6],[31] [18-MC-8],[29] [30-MC-10],[32] and stacking metallacrowns[33−35] as well as a variety of dimers and fused metallacrowns[21,27,36,37] have been reported to date. Cryptates, calixarenes, and molecular box motifs with metal ions replacing carbon atoms at the core can also act as inorganic molecular hosts capable of selectively binding cationic, anionic, and neutral guests.[38−44]

For 12-MC-4 metallacrowns, two structural motifs have been reported: regular and inverse. For the regular motif, the metallacrown ring shows the repeating pattern [−O−N−M−] with the oxygen atoms oriented toward the center of the cavity. For the inverse motif, while the repeating pattern [−O−N−M−] remains the same, now the metal atoms are oriented toward the center of the cavity. The regular metallacrown binds cations in a central cavity while the inverse metallacrown can bind anions. These compounds show similarities with, apart from 12-C-4 crown ethers, metal complexes of porphyrins or phthalocyanines concerning the structural characteristics, cavity size, and bite distance giving a new perspective on these compounds as host molecules.

In this paper, we report the synthesis, characterization, and crystal structure of the uninuclear Zn(Hpko)Cl$_2$ (**1**), the 12-membered metallacrown (OH)$_2$[inv12-MC$_{Zn(II)N(pko)}$-4]Cl$_2$ (**2**), and the octanuclear 12-membered metallacrown [Zn$_2$]{[Zn$_2$(pko)$_4$][12-MC$_{Zn(II)N(shi)}$-4](CH$_3$OH)$_2$} (**3**). Compound **3** is a particularly interesting molecule because it is the first example of a metallacrown with binuclear units.

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(7) The nomenclature for metallacrowns is as follows: M′$_m$A$_a$[X-MC$_{M(ox)H(z)}$-Y], where X and Y indicate ring size and number of oxygen donor atoms, MC specifies a metallacrown, M and ox are the ring metal and its oxidation state, H is the identity of the remaining heteroatom bridge, and (z) is an abbreviation for the organic ligand containing the N/O functionality. There are *m* captured metals (M′) and *a* bridging anions (A) bound to the ring oxygens and metals, respectively. For the metallacrowns characterized as "inverse", the nomenclature proposed is similar except the meaning of Y, indicating the number of metal ions oriented toward the central cavity.

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Experimental Section

Abbreviations. H_3shi, salicylhydroxamic acid; Hpko, di-2-pyridyl-ketonoxime.

Materials. The chemicals for the synthesis of the compounds were used as purchased. Dimethylformamide (dmf) was distilled from calcium hydride (CaH_2), and CH_3OH, from magnesium (Mg), and these were stored over 3 Å molecular sieves. H_3shi, Hpko, and $ZnCl_2$ were purchased from Aldrich Co. All chemicals and solvents were reagent grade.

Synthesis of the Compounds. Zn(Hpko)Cl_2 (1). A 1 mmol portion of $ZnCl_2$ (0.136 g) was dissolved in 50 mL of methanol, and 1 mmol of di-2-pyridyl-ketonoxime (0.199 g) was added. The mixture was stirred for 1 h. Colorless crystals suitable for X-ray diffraction studies were obtained by slow evaporation of the mother liquid over a few days. Yield 70%. Analytical data: fw = 335.48. Found: C, 39.42; H, 2.75; N, 12.58; Zn, 19.20. $C_{11}H_9Cl_2N_3OZn$ requires C, 39.38; H, 2.70; N, 12.52; Zn, 19.37. IR (KBr pellet, cm^{-1}): $(C{=}N)_{pko}$, 1600(vs); $(N{-}O_{ox})_{pko}$, 1286(s).

$(OH)_2$[inv12-$MC_{Zn(II)N(pko)}$-4]Cl_2·1.4dmf·1.4CH_3OH (2). A 2 mmol portion of $ZnCl_2$ (0.272 g) was dissolved in 50 mL of methanol, and di-2-pyridyl-ketonoxime (0.398 g, 2 mmol) deprotonated by NaOH (0.12 g, 3 mmol) in 50 mL CH_3OH was added. The mixture was stirred for 1 h until the solution color became pale yellow. By addition of 5 mL of dmf, colorless crystals suitable for X-ray diffraction studies were obtained by slow evaporation of the mother liquid over a few days. Yield 60%. Analytical data: fw = 1306.41. Found: C, 45.50; H, 3.80; N, 14.30; Zn, 20.00. $C_{49.6}H_{49.4}Cl_2N_{13.4}O_{8.8}Zn_4$ requires C, 45.60; H, 3.81; N, 14.36, Zn, 20.01. IR (KBr pellet, cm^{-1}): (O—H), 3436(s); $(C{=}N)_{pko}$, 1595(vs); $(N{-}O_{ox})_{pko}$, 1262(s).

[$Zn_4(pko)_4$][12-$MC_{Zn(II)N(shi)}$-4]$(CH_3OH)_2$·6.8CH_3OH (3). A 2 mmol portion of $ZnCl_2$ (0.272 g) was dissolved in 50 mL of methanol and salicylhydroxamic acid (0.153 g, 1 mmol), and di-2-pyridyl-ketonoxime (0.199 g, 1 mmol) deprotonated by NaOH (0.16 g, 4 mmol) in 50 mL CH_3OH was added. The mixture was stirred for 1 h until the solution color became yellow. Yellow crystals suitable for X-ray diffraction studies were obtained by slow evaporation of the mother liquid over a few days. Yield 60%. Analytical data: fw = 2198.19. Found: C, 44.24; H, 3.90; N, 10.05; Zn, 23.60. $C_{80.8}H_{83.2}N_{16}O_{24.8}Zn_8$ requires C, 44.14; H, 3.81; N, 10.19; Zn, 23.79. IR (KBr pellet, cm^{-1}): $(C{=}N)_{pko}$, 1597(vs); $(C{=}N)_{shi}$, 1575(vs); $(C{=}O_{ph})_{shi}$, 1469(s); $(C{=}O_{ox})_{shi}$, 1438(s); $(N{-}O_{ox})_{shi,pko}$, 1259(s).

Physical Measurements. Infrared spectra (200−4000 cm^{-1}) were recorded on a Perkin-Elmer FT-IR 1650 spectrometer with samples prepared as KBr pellets. UV−vis spectra were recorded on a Shimadzu-160A dual beam spectrophotometer. C, H, and N elemental analyses were performed on a Perkin-Elmer 240B elemental analyzer; Zn was determined by atomic absorption spectroscopy on a Perkin-Elmer 1100B spectrophotometer. Electric conductance measurements were carried out with a WTW model LF 530 conductivity outfit and a type C cell, which had a cell constant of 0.996. This represents a mean value calibrated at 25 °C with potassium chloride. A Crison basic 20 pH-meter was used for pH measurements.

Table 1. Crystal Data and Structure Refinement for **1**, **2**, and **3**

	1	**2**	**3**
empirical formula	$C_{11}H_9Cl_2N_3OZn$	$C_{49.6}H_{45.4}Cl_2$-$N_{13.4}O_{8.8}Zn_4$	$C_{80.8}H_{83.2}N_{16}$-$O_{24.8}Zn_8$
fw	335.48	1302.38	2198.19
T (K)	298	298	298
wavelength (Å)	Mo Kα 0.71073	Cu Kα 1.54180	Mo Kα 0.71073
cryst syst	triclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a (Å)	7.295(9)	11.826(5)	15.220(9)
b (Å)	12.71(1)	17.739(6)	16.382(9)
c (Å)	14.20(1)	15.680(5)	21.31(1)
α (deg)	88.55(3)		96.76(2)
β (deg)	82.75(4)	91.62(1)	110.16(2)
γ (deg)	89.78(4)		104.99(2)
V (Å^3)	1305(3)	3288(2)	4691(5)
Z	4	2	2
d (calcd) (Mg/m^3)	1.707	1.308	1.556
abs coeff μ (mm^{-1})	2.280	2.866	2.089
octants collected	$\pm h, \pm k, -l$	$\pm h, k, -l$	$\pm h, \pm k, l$
GOF on F^2	1.106	0.985	1.135
final R [$I > 2\sigma(I)$]	R1 = 0.0986 wR2 = 0.2621[a]	R1 = 0.0511 wR2 = 0.1440[b]	R1 = 0.0512 wR2 = 0.1342[c]

[a] For 2483 reflections with $I > 2\sigma(I)$. [b] For 3932 reflections with $I > 2\sigma(I)$. [c] For 9316 reflections with $I > 2\sigma(I)$.

X-ray Crystal Structure Determination of 1, 2, and 3. Colorless crystals of **1**, **2**, and **3** with approximate dimensions of 0.10 × 0.25 × 0.45 mm^3, 0.15 × 0.17 × 0.50 mm^3, and 0.10 × 0.20 × 0.40 mm^3, respectively, were mounted in capillaries. Diffraction measurements for **1** and **3** were made on a Crystal Logic dual goniometer diffractometer using graphite monochromated Mo radiation, while for **2** data collection was performed on a $P2_1$ Nicolet diffractometer, upgraded by Crystal Logic, using graphite monochromated Cu radiation. Crystal data and parameters for data collection are reported in Table 1. Unit cell dimensions were determined and refined by using the angular settings of 25 automatically centered reflections in the range 11° < 2θ < 23°(for **1** and **3**) and 22° < 2θ < 54° (for **2**). Intensity data were recorded using $\theta-2\theta$ scan. Three standard reflections monitored every 97 reflections showed <3.0% intensity fluctuation. Lorentz polarization corrections were applied using Crystal Logic software. Scattering factors were taken from the International Tables for X-ray Crystallography.[45] The structure was solved by direct methods using the programs SHELXS-86[46] and refined by full-matrix least-squares techniques on F^2 with SHELXL-93.[47] Further crystallographic details for **1**: $2\theta_{max} = 43°$, scan speed 2.7°/min, scan range 2.4° + $\alpha_1\alpha_2$ separation, reflections collected/unique/used = 3155/3002(R_{int} = 0.0408)/3002, parameters refined = 329, F(000) = 672, R1/wR2 (all data) = 0.1120/0.2808, $[\Delta\rho]_{max}/[\Delta\rho]_{min}$ = 1.221/−1.630, $[\Delta/\sigma]_{max}$ = 0.009. All H atoms were introduced at calculated positions as riding on bonded atoms and were refined isotropically; all non-H atoms were refined anisotropically. Further crystallographic details for **2**: $2\theta_{max} = 130°$, scan speed 3.0°/min, scan range 2.7° + $\alpha_1\alpha_2$ separation, reflections collected/unique/used = 4677/4504(R_{int} = 0.0159)/4504, parameters refined = 409, F(000) = 1322.4, R1/wR2 (all data) = 0.0584/0.1570, $[\Delta\rho]_{max}/[\Delta\rho]_{min}$ = 0.761/−0.412, $[\Delta/\sigma]_{max}$ = 0.971. The H atoms were located by difference maps and were refined isotropically (except those on C11, C28, C29, and C31 which were introduced at calculated positions as riding on bonded atoms). All the non-H atoms of the metallacrown and N and O atoms of the dmf solvent were refined anisotropically; the C atoms of the dmf and the methanols were refined isotropically. Further crystallographic details for **3**: $2\theta_{max}$ = 46.5°, scan speed 2.6°/min, scan range 2.1° + $\alpha_1\alpha_2$ separation, reflections collected/unique/used = 13201/12794(R_{int} = 0.0197)/12793, parameters refined = 1253, F(000) = 2237, R1/wR2 (all data) = 0.0830/0.1530, $[\Delta\rho]_{max}/[\Delta\rho]_{min}$ = 1.089/−0336, $[\Delta/\sigma]_{max}$

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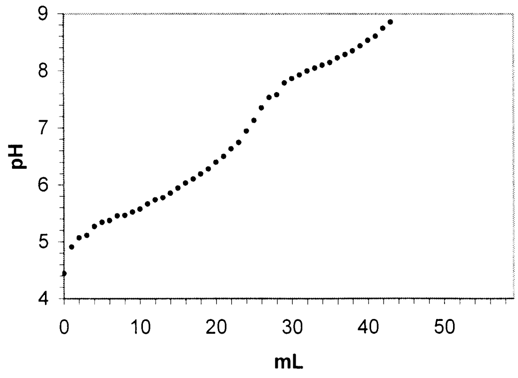

Figure 1. Potentiometric titration curve for the reaction 2.

= 0.067. All H atoms of the metallacrown were introduced at calculated positions as riding on bonded atoms and were refined isotropically; no H atoms for the solvent molecules were included in the refinement. All non-H atoms were refined anisotropically.

Results and Discussion

Synthesis of the Complexes. The synthesis of the Zn(Hpko)Cl_2 (**1**) was achieved via the reaction of $ZnCl_2$ with di-2-pyridyl-ketonoxime in methanol.

$$ZnCl_2 + Hpko \rightarrow Zn(Hpko)Cl_2 \qquad (1)$$

The compound is a colorless, crystalline solid, is soluble in dmso, dmf, methanol, and H_2O, and is not electrolyzed in methanol and H_2O.

The synthesis of the inv-12-membered metallacrown was achieved by the reaction of $ZnCl_2$ with the sodium salt of di-2-pyridyl-ketonoxime in methanol/dmf or by addition of NaOH in a MeOH/dmf solution of **1**:

$$4Zn(Hpko)Cl_2 + 6NaOH \leftrightarrows (OH)_2[inv12\text{-}MC_{Zn(II)N(pko)}\text{-}4]Cl_2 + 6NaCl + 4H_2O \qquad (2)$$

The compound is a colorless, crystalline solid and is insoluble in dmf, dmso, methanol, and H_2O.

This reaction was studied by acid−base potentiometric titration (Figure 1). Zn(Hpko)Cl_2 [0.25 mmol (0.083 g)] was dissolved in 25 mL of H_2O/MeOH 1:1, and 0.01 M NaOH was added in 1 mL increments. The potentiometric titration curve, with a mother solution of pH = 4.5, shows a change of the slope at pH = 8 while a white precipitate started to deposit that, by the completion of the titration, has been characterized by IR and elemental analysis having the formula of the inv-metallacrown. By the addition of 37.5 mL of NaOH, the slope of the curve changes again indicating the completion of the conversion to inv-metallacrown. This reaction is reversible, and by addition of HCl, the white solid dissolved. The solution was reduced in volume, and the crystalline solid deposited was characterized with the formula of **1**.

The synthesis of $[Zn_4(pko)_4][12\text{-}MC_{Zn(II)N(shi)}\text{-}4](CH_3OH)_2$ was achieved by the reaction of $ZnCl_2$, salicylhydroxamic acid, and di-2-pyridyl-ketonoxime with the presence of sodium hydroxide in methanol:

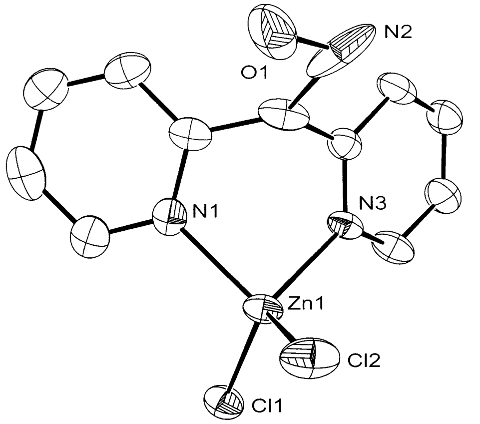

Figure 2. ORTEP view of complex **1** with 50% thermal ellipsoids with only the heteroatoms labeled.

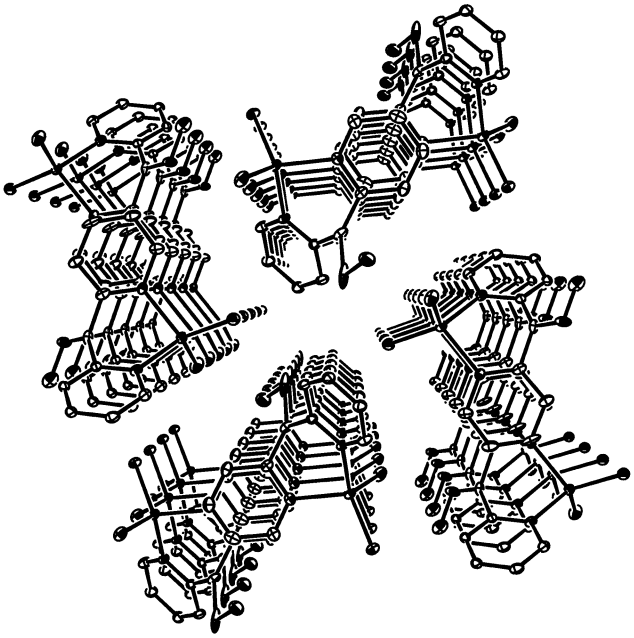

Figure 3. Packing diagram of **1** along the *a* axis.

$$8ZnCl_2 + 4H_3shi + 4Hpko + 16NaOH \rightarrow [Zn_4(pko)_4][12\text{-}MC_{Zn(II)N(shi)}\text{-}4](CH_3OH)_2 + 16NaCl + 16H_2O \qquad (3)$$

The compound is a yellowish, crystalline solid, soluble in dmf and dmso, and there is no electrolyte in these solvents.

Description of Structure Zn(Hpko)Cl_2 (1). The ORTEP diagram of Zn(Hpko)Cl_2 (**1**) is presented in Figure 2. Important bond distances and angles are presented in Table 2. The zinc atom is in a distorted tetrahedral environment with a Hpko ligand bound to the metal ion in a chelate fashion through the two pyridyl nitrogens. The protonated ketonoximate moiety remains unbound. The angles around the zinc ion vary from 91.8(4)° to 117.6(2)° with the smallest one between the nitrogen atoms and the largest one between the chloride ions. The chelate six-membered ring is not planar. The average dihedral angle[48] $\Pi_{C(7)C(6)Zn(1)N(3)}-C(6)Zn(1)-\Phi_{C(5)C(6)Zn(1)N(1)}$ was about 134.3° considering the two

Table 2. Selected Bond Distances (Å) and Angles (deg) of Zn(Hpko)Cl_2 (**1**)

Distances			
Zn(1)−N(1)	2.05(1)	Zn(1)−Cl(2)	2.201(4)
Zn(1)−N(3)	2.05(1)	Zn(1)−Cl(1)	2.219(4)
Angles			
N(1)−Zn(1)−N(3)	91.8(4)	N(1)−Zn(1)−Cl(1)	109.1(3)
N(1)−Zn(1)−Cl(2)	111.7(3)	N(3)−Zn(1)−Cl(1)	112.9(3)
N(3)−Zn(1)−Cl(2)	110.8(3)	Cl(2)−Zn(1)−Cl(1)	117.6(2)

Table 3. Selected Bond Distances (Å) and Angles (deg) of $(OH)_2$[inv12-$MC_{Zn(II)N(pko)}$-5]Cl_2 (**2**)

Distances			
Zn(2)−N(21)$_{pyridyl}$	2.185(4)	Zn(1)−O(21)$_{ketonoxamato}$	1.964(3)
Zn(2)−N(23)$_{ketonoxamato}$	2.135(4)	Zn(1)−O(1)$_{ketonoxamato}$	1.956(3)
Zn(2)−N(1)#$_{pyridyl}$	2.170(4)	Zn(1)−Cl	2.207(2)
Zn(2)−N(3)#$_{ketonoxamato}$	2.153(3)	Zn(1)−O(2)$_{hydroxo}$	1.963(5)
Zn(2)−O(2)$_{hydroxo}$	2.124(7)	Zn(2)···Zn(2)#	3.231(1)
Zn(2)−O(2)#$_{hydroxo}$	2.112(6)	Zn(2)···Zn(1)#	3.326(1)
Angles			
O(1)−Zn(1)−O(2)	103.5(2)	O(2)−Zn(2)−N(21)	160.1(2)
O(1)−Zn(1)−O(21)	101.6(1)	O(2)#1−Zn(2)−O(2)	80.6(2)
O(2)−Zn(1)−O(21)	102.5(2)	Zn(2)#1−O(2)−Zn(2)	99.4(2)
O(1)−Zn(1)−Cl	112.7(1)	Zn(1)−O(2)−Zn(2)	109.3(3)
O(2)−Zn(1)−Cl	122.9(2)	Zn(1)−O(2)−Zn(2)#1	109.4(3)
O(21)−Zn(1)−Cl	111.2(1)	H−O(2)−Zn(2)#	108.8
N(23)−Zn(2)−N(3)#1	160.4(1)	H−O(2)−Zn(2)	104.1
O(2)#1−Zn(2)−N(1)#1	158.4(2)	H−O(2)−Zn(1)	123.0

C(7)−C(6)−Zn(1)−N(3) and C(5)−C(6)−Zn(1)−N(1) planes as planar (2.5° the largest off plane dihedral angle). Despite the presence of a protonated oxamato group, a hydrogen bonding intra- or intermolecular interaction was not detected. There are two molecules per asymmetric unit as shown in the packing diagram (Figure 3).

Description of the Structure $(OH)_2$[inv12-$MC_{Zn(II)N(pko)}$-4]Cl_2 (2). The ORTEP diagram of the metallacrown $(OH)_2$[inv12-$MC_{Zn(II)N(pko)}$-4]Cl_2 (**2**) is presented in Figure 4. Important bond distances and angles are presented in Table 3. The structure contains a crystallographic inversion center located in the center of the binuclear unit [$Zn_2(OH)_2$]. The metallacrown core is characterized as "inverse" because the zinc atoms, rather than oxygen atoms, are oriented toward the central cavity. This compound is analogous to that characterized as "inverse" metallacrown,[26] $(OH)_2$[inv12-$MC_{Zn(II)N(pko)}$-4]$(CH_3COO)_2$, or "inverse" crowns.[49−56] The zinc atoms show two coordination geometries. Zn(1) and Zn(1)# are in distorted tetrahedral environment with angles around zinc ions varying between 101.6(2)° and 122.9(2)°. Zn(1) and Zn(1)# are bound to one of the μ_3-bridging hydroxides (O(2) and O(2)#) and to two ketonoxamato oxygens (O(1), O(21), O(1)#, and O(21)#) of the pko^- ligand. The fourth site of the tetrahedron is occupied by a coordinated chloride ion. The octahedral zinc atoms (Zn(2), Zn(2)#) are bound to two pko^- ligands by pyridyl nitrogens (N(1), N(21), N(1)#, and N(21)#) and the oxamato nitrogens (N(3), N(23), N(3)#, and N(23)#) in five-membered chelate rings. The remaining two coordination sites of the octahedron are filled by two μ_3-bridging hydroxides (O(2) and O(2)#) accommodated in the center of the metallacrown ring. The ligands form a propeller configuration that imposes absolute stereoisomerism with Λ chirality on Zn(2) and Δ chirality on Zn(2)#. The two hydroxo oxygens (O(2) and O(2)#) bridge to two octahedral zinc atoms and one tetrahedral zinc atom, Zn(1) and Zn(2), respectively. The coordination geometry around the oxygen atoms can be characterized as distorted tetrahedral (the sum of angles around O(2) and the trigonal planes of the tetrahedron varies from 312.2° to 341.7°), while the Zn(2)−O(2)−Zn(2)#−O(2)# core is planar as it is restricted by the presence of a crystallographic inversion center.

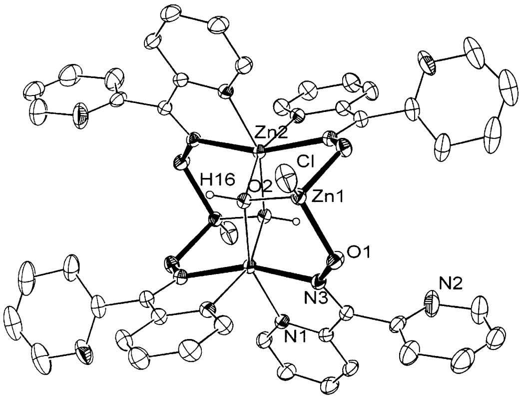

Figure 4. ORTEP view of compound **2** with 30% thermal ellipsoids with only the heteroatoms labeled.

General Description of the Mixed Ligand [12-$MC_{M(x)N(shi)2(pko)2}$-4] Metallacrowns. As mentioned previously, a series of mixed ligand metallacrowns with unique characteristics has been obtained using di-2-pyridyl-ketonoxime in conjunction with salicylic hydroxamic acid. A 2:2 distribution of shi^{3-} and pko^- results in a M(II) neutral metallacrown ring while 3:1 stoichiometry of shi^{3-} and pko^- results in a dianion M(II) metallacrown. The metallacrown charge may also be adjusted by mixing the ring metals. Thus, the shi^{3-}/pko^- (2:2) with alternating M(II) and M(III) gives the 2^+ metallacrown.[21]

Description of the Structure $Zn_8(shi)_4(pko)_4(CH_3OH)_2$ (3). The colored ORTEP diagram of **3** is presented in Figure 6. Important bond distances and angles are presented in Table 4. The octanuclear cluster $Zn_8(shi)_4(pko)_4(CH_3OH)_2$ contains a 12-membered metallacrown core constructed by four Zn metal atoms, Zn(3), Zn(5), Zn(7), and Zn(8), and four shi^{3-}

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(48) The nomenclature used for the dihedral angles is described as follows: $\Pi_{C(7)C(6)Zn(1)N(3)}$ specifies the level that is formed with the indicated atoms, C(6)Zn(1) indicates the common side of the two levels, and $\Phi_{C(5)C(6)Zn(1)N(1)}$ specifies the second level with the indicated atoms.

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Table 4. Selected Bond Distances (Å) and Angles (deg) of $Zn_2\{[Zn_2(pko)_4][12\text{-}mc_{Zn(II)N(shi)}\text{-}4](CH_3OH)_2\}$ (**3**)

accommodated $Zn(1)_{octahedral}$		accommodated $Zn(4)_{tetrahedral}$	
$Zn(1)-O_{ketonoxamato-pko}$	2.025(5)	$Zn(4)-O_{ketonoxamato-pko}$	1.928(5)
$Zn(1)-O_{ketonoxamato-pko}$	2.036(5)	$Zn(4)-O_{ketonoxamato-pko}$	1.931(5)
$Zn(1)-O_{oxamato-shi}$	2.091(5)	$Zn(4)-O_{oxamato-shi}$	1.975(5)
$Zn(1)-O_{oxamato-shi}$	2.105(5)	$Zn(4)-O_{oxamato-shi}$	1.977(4)
$Zn(1)-O_{oxamato-shi}$	2.245(5)		
$Zn(1)-O_{oxamato-shi}$	2.365(5)		
[ring $Zn(7)_{mono}$ and $Zn(8)_{mono}]_{pyramidal}$		[ring $Zn(3)_{bi}$ and $Zn(5)_{bi}]_{octahedral}$	
$[Zn_{mono}-O_{carbonyl-shi}]_{av}$	1.965	$[Zn_{bi}-N_{oxamato-shi}]_{av}$	2.049
$[Zn_{mono}-O_{phenolato-shi}]_{av}$	2.022	$[Zn_{bi}-O_{phenolato-shi}]_{av}$	2.035
$[Zn_{mono}-N_{oxamato-shi}]_{av}$	2.097	$[Zn_{bi}-N_{ketonoxamato-pko}]_{av}$	2.119
$[Zn_{mono}-N_{pyridyl-pko}]_{av}$	2.154	$[Zn_{bi}-O_{MeOH}]_{av}$	2.145
		$[Zn_{bi}-N_{pyridyl-pko}]_{av}$	2.170
		$[Zn_{bi}-O_{oxamato-shi}]_{av}$	2.292
[biunits Zn(2) and $Zn(6)]_{pyramidal}$		Zn···Zn separation in biunits	
$[Zn_{biunit}-O_{carbonyl-shi}]_{av}$	1.956	Zn(1)−Zn(4)	3.055(2)
$[Zn_{biunit}-O_{phenolato-shi}]_{av}$	2.029	Zn(2)−Zn(3)	3.003(2)
$[Zn_{biunit}-N_{ketonoxamato-pko}]_{av}$	2.064	Zn(5)−Zn(6)	3.043(2)
$[Zn_{biunit}-O_{oxamato-shi}]_{av}$	2.124		
$[Zn_{biunit}-N_{pyridyl-pko}]_{av}$	2.105		
Angles			
O(51)−Zn(1)−O(11)	172.7(2)	O(71)−Zn(4)−O(11)	120.5(2)
O(41)−Zn(1)−O(21)	169.0(2)	O(21)−Zn(4)−O(11)	97.9(2)
O(1)−Zn(1)−O(31)	159.8(2)	O(23)−Zn(5)−N(62)	164.4(2)
O(32)−Zn(2)−N(42)	130.4(2)	N(21)−Zn(5)−N(61)	165.6(2)
O(31)−Zn(2)−N(41)	170.6(2)	OM2−Zn(5)−O(1)	176.1(2)
N(11)−Zn(3)−N(71)	167.1(2)	O(2)−Zn(6)−N(52)	133.6(2)
O(13)−Zn(3)−N(72)	164.7(2)	N(51)−Zn(6)−O(1)	172.6(2)
OM1−Zn(3)−O(31)	174.0(2)	O(22)−Zn(7)−N(31)	132.8(2)
O(61)−Zn(4)−O(71)	111.4(2)	O(33)−Zn(7)−O(21)	176.0(2)
O(61)−Zn(4)−O(21)	121.7(2)	O(12)−Zn(8)−N(1)	139.0(2)
O(61)−Zn(4)−O(11)	104.6(2)	O(3)−Zn(8)−O(11)	169.5(2)
O(71)−Zn(4)−O(21)	101.3(2)		

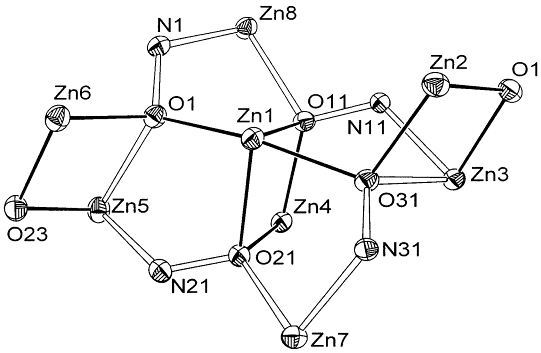

Figure 5. ORTEP view of the metallacrown part of compound **3** with 30% thermal ellipsoids of the atoms showing the connectivity pattern.

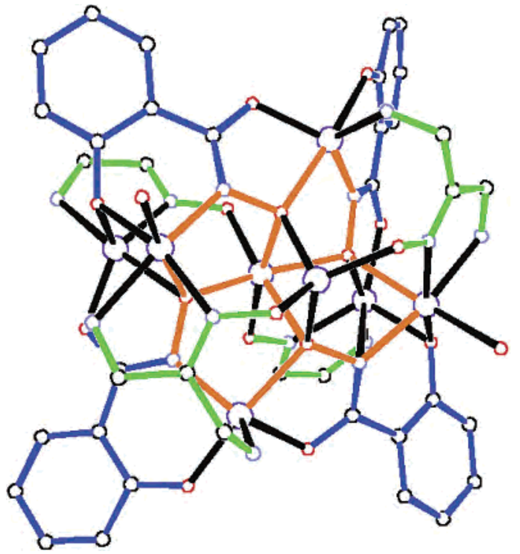

Figure 6. Colored diagram of **3** showing (a) in orange the metallacrown ring; (b) in blue the coordination of shi ligands; (c) in green the coordination of pko ligands; and (d) in black the two methanol molecules. Also, large purple circles = Zn; cyan circles = nitrogens; red circles = oxygens; black circles = carbons; the pyridyl ring of pko ligands have been omitted for clarity

ligands. Therefore, a part of the cluster can be described having the formally anionic $[12\text{-}MC_{Zn(II)N(shi)}\text{-}4]^{4-}$ core. The specific connectivity of the atoms forming the ring is Zn(3)−O(31)−N(31)−Zn(7)−O(21)−N(21)−Zn(5)−O(1)−N(1)−Zn(8)−O(11)−N(11). The metallacrown core is severely distorted from planarity, showing a saddle shaped arrangement. Two of the zinc atoms, Zn(3) and Zn(5), are in an octahedral coordination environment while for the other two, Zn(7) and Zn(8), the geometry is best described as distorted trigonal bipyramidal. The distortion of the ideal geometry described by the trigonality index,[57] $\tau = (176.00-132.84)/60 = 0.72$ for Zn(7) and $\tau = (169.48-138.99)/60 = 0.50$ for Zn(8) ($\tau = 0$ denotes perfect square pyramidal; $\tau = 1$ denotes perfect trigonal bipyramidal), shows distortion away from the regular square-based pyramidal geometry. The metallacrown core accommodates a binuclear compound with the formula $[Zn_2(pko)_4]$, and now, the formula can be written as $\{[Zn_2(pko)_4][12\text{-}MC_{Zn(II)N(shi)}\text{-}4](CH_3OH)_2\}^{4-}$. In the binuclear unit, a zinc metal ion, Zn(1), is in octahedral coordination geometry, and the second one, Zn(4), in tetrahedral coordination geometry. The tetrahedral Zn(4) is bound to two oxygen atoms of the metallacrown ring, O(11) and O(21), while it is bridged to Zn(3) and Zn(5) ring atoms through ketonoxamato moieties of two pko^{1-} ligands. The octahedral Zn(1) is bound to four ring oxygens, O(1), O(11), O(21), O(31), and is bridged to two zinc ions not participating in the metallacrown ring, Zn(2) and Zn(6), through ketonoxamato moieties of two pko^- ligands. The Zn(1)−O(11)−O(21)−Zn(4) unit is almost coplanar with a dihedral angle of 177.4° while Zn···Zn separation is 3.055 Å. A binuclear host molecule has also been reported for the compound $[Mn(II)_2(2,4\text{-}DP)_2(HCOO)_2][12\text{-}MC_{Mn(III)N(shi)}\text{-}4]\text{-}(py)_6$,[27] but in this compound, the host binuclear unit was above the plane of the almost planar metallacrown ring. In the present compound, one zinc atom lies above the average plane of the ring zinc atoms, and the second one lies below (Figure 5). The Zn(2) and Zn(6) metal ions create binuclear units with Zn(3) and Zn(5), respectively, with two oxamato oxygens, O(1) and O(31), and two phenolato oxygens, O(23) and O(13), of the four interlinked shi^{3-} ligands acting as bridging atoms. The Zn(2)−O(13)−O(31)−Zn(3) and Zn(5)−O(1)−O(23)−Zn(6) units are almost coplanar with dihedral angles of 179.3° and 176.7°, respectively, while the Zn···Zn and O···O separations, Zn(2)···Zn(3) = 3.003 Å, O(13)···O(31) = 2.973 Å and Zn(5)···Zn(6) = 3.043 Å, O(1)···O(23) = 2.963 Å, support a square planar geometry of the binuclear units. The geometry about Zn(2) and Zn(6) is best described as distorted trigonal bipyramidal. The

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trigonality index, $\tau = (170.6-130.4)/60 = 0.67$ for Zn(2) and $\tau = (172.6-133.6)/60 = 0.65$ for Zn(6), shows distortion away from the regular square-based pyramidal geometry. The complete formula of the cluster can be written as $Zn_2\{[Zn_2(pko)_4][12\text{-}MC_{Zn(II)N(shi)}\text{-}4](CH_3OH)_2\}$ (Figure 6).

Conclusion. While 12-MC-4 metallacrowns have been reported previously, some very interesting features are presented in this report. Compound **2** is a rare example of a structurally characterized 12-MC-4 compound that has been characterized as an "inverse" metallacrown with the zinc atoms, rather than oxygen atoms, oriented toward the central cavity, and it can accommodate anions in the center of the metallacrown ring. Compound **3** is the first zinc metallacrown having the "regular" $[12\text{-}MC_{Zn(II)N(shi)}\text{-}4]^{4-}$ core. The 12-membered ring acts as host agent for a binuclear compound while two of the ring metal ions create binuclear units with zinc ions.

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Supporting Information Available: Crystallographic information in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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