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# Synthesis and Crystal Structure of the First Inverse 12-Metallacrown-4

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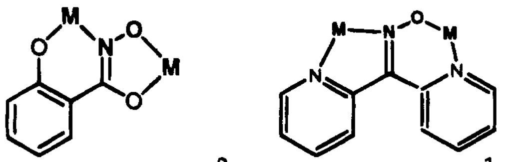
Metallacrowns are a new class of multinuclear clusters that are analogous to crown ethers in both structure and function.[1] Structurally, metallacrowns resemble crown ethers in their repeating pattern of O−X−X−O with the oxygen atoms oriented toward the center of a cavity.[2] Functionally, both metallacrowns and crown ethers are able to encapsulate cations[3] and simultaneously bind anions.[4] In general, metallacrowns are synthesized using the ligand salicylhydroxamic acid which provides four heteroatoms for binding as shown in Chart 1. One metal can bind to the iminophenolate, a six-membered chelate ring, and a second metal binds to hydoximate oxygens in a five-membered chelate ring. The metals repeat this type of binding to give a cyclic 12-MC-4[5] structure where the M−N−O−M linkage defines the ring (M = $Mn^{3+}$, $Cu^{2+}$, $Ni^{2+}$, $Ga^{3+}$, $Fe^{3+}$).[6] The metallacrowns possibly offer advantages over organic crown ethers in that the incorporation of metals, in ring positions as well as in the cavity, provides interesting magnetic, spectrophotometric, and redox properties. Thus, through peripheral organic ligand modification,[7] metallacrowns have the potential for applications as chemically modified electrodes, anion-selective separation agents, and precursors for liquid crystalline or inorganic polymer chemistry. We have investigated the coordination chemistry of this new molecular class with a variety of hydroxamate ligands.[6a] As shown in Chart 1, bis(2-pyridyl) ketone oxime (Hpko) has the same number of heteroatoms and five- and six-membered chelates necessary for metallacrown ring formation as does $H_3$shi. While classical metallacrowns bind cations in a central cavity, one might question whether anions could be encapsulated in a preformed cavity by inverting the atom connectivity so that the metal atoms are oriented toward the center of the cavity. Such complexes would be analogous to Hawthorne's pioneering efforts with anti-crowns.[8] We report here the first example of a 12-metallacrown-4 that realizes an "anti-metallacrown" structure type *inv*(OH)$_2$[12-MC$_{\mathrm{Zn^{2+}N(pko)}}$-4], **1**, by using an oxime based ligand.[9]

**Chart 1**



Binding Sites of shi$^{-3}$ Binding Sites of pko$^{-1}$

The complex, **1**, was synthesized with 0.55 g (2.5 mmol) of $Zn(OAc)_2$ and 0.40 g (2 mmol) of bis(2-pyridyl) ketone oxime in 75 mL of dimethylformamide. The solution was stirred for 24 h, and then crystals were obtained (42% yield) from this solution by vapor diffusion with ether after 3 days. One of these colorless rectangular crystals was selected for X-ray crystal analysis.[10] The preparation of an inverse metallacrown is a direct consequence of the substitution of an oxime ligand for the previously employed hydroxamate ligands. **1** has a net positive charge since the ligand has a charge of 1− while the Zn is divalent. The net positive charge is balanced by the binding of two hydroxides and two acetates resulting in an overall charge neutral metallacrown.

An ORTEP diagram of **1** is shown in Figure 1 with the metallacrown ring outlined in bold. Important bond lengths and angles are provided in the figure captions. The structure has a crystallographic inversion center with two Zn atoms, Zn1 and Zn1a, in distorted octahedral environments and two Zn atoms, Zn2 and Zn2a, in severely distorted polyhedra. The octahedral zinc ions are bound to two pko$^-$ ligands by pyridyl nitrogens (N5, N1, N5a, N1a) and the oxime nitrogens (N4, N2, N4a, N2a) in two five-membered chelate rings. The other two coordination sites are filled by two bound, triply bridging hydroxides (O2, O2a) in the center of the ring. The ligands form a propeller configuration that imposes absolute stereoisomerism with Λ chirality on Zn1 and Δ chirality on Zn1a.[11] The second set of zinc ions are bound to one of the bridging hydroxides and to two oxime oxygens(O1, O3, O1a, O3a) of the ligand. Fourth and fifth sites are occupied by oxygens from a coordinated acetate. As shown in Figure 2, one oxygen (O4) forms a strong bond with Zn2 (1.92 Å) while the second oxygen

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(5) Nomenclature: A naming system was developed for the metallacrowns that resembles the nomenclature used for crown ethers. An organic crown ether has the name 9-crown-3 where 9 refers to the total number of ring atoms and 3 refers to the number of ether oxygens. A similar metallacrown would be named 9-MC$_{\mathrm{M^{n+}N}}$-3, where MC means metallacrown, $M^{n+}$ is the metal ion and oxidation state used in the ring, and N is nitrogen. The metallacrowns usually have encapsulated ions which are named first. For instance, a metallacrown with two encapsulated sodium ions and bridging chlorides is named (NaCl)$_2$-[12-MC$_{\mathrm{M^{3+}N}}$-4]. Since metallacrowns have been synthesized with different ligands, the name is further specified with a three-letter abbreviation of the ligand after the N, (NaCl)$_2$[12-MC$_{\mathrm{M^{3+}N(shi)}}$-4] where shi stands for salicylhydroxamic acid. *inv* is used as a prefix to specify an inverse metallacrown.

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(9) The more appropriate nomenclature would be to call these anti-metallacrowns by analogy to Hawthorne's complexes; however, we prefer "inverse" in this system because anti has a specific stereochemical meaning in these complexes (syn versus anti of the bridging anion) that is not applicable to simple crown ether chemistry.

(10) *inv*(OH)$_2$[12-MC$_{\mathrm{Zn^{2+}N(pko)}}$-4] crystallized as colorless rectangular blocks. This triclinic crystal was solved in the $P\bar{1}$ (No. 2) space group with unit cell dimensions of $a$ = 10.811(2) Å, $b$ = 11.771(2) Å, $c$ = 12.005(2) Å, α = 104.17(1)°, β = 109.34(1)°, γ = 102.81(1)°, and $V$ = 1318.7(4) Å$^3$ and with $Z$ = 1. Mo Kα radiation, λ = 0.71073 Å, was used. A full sphere of data, to 2Θ = 52° was used (11 341 reflections, 5213 unique). The structure was solved with SHELXTL PLUS, SHELXL-93 using direct methods. A semiempirical absorption correction was used. The full-matrix least-squares refinement on $F^2$ reached R = 0.046, wR2 = 0.1388. All calculations were performed on a VAXStation 3500. Anal. Calcd for $Zn_4C_{48}H_{40}N_{12}O_8$: C, 46.55; H, 3.26; N, 13.57; Zn, 21.1. Found: C, 46.66; H, 3.82; N, 13.63; Zn, 20.6. An ESI mass spectrum of **1** in methanol gave peaks at 1187 (30% base) and 1128 (10% base) for *inv*(OH)$_1$[12-MC$_{\mathrm{Zn^{2+}N(pko)}}$-4] and for *inv*(OH)$_1$[12-MC$_{\mathrm{Zn^{2+}N(pko)}}$-4] without one acetate, respectively.

(11) The Λ and Δ isomers are defined using a skew line convention for compounds with a $C_2$ or pseudo-$C_2$ axis as described in *Inorg. Chem.* **1970**, 9, 1.

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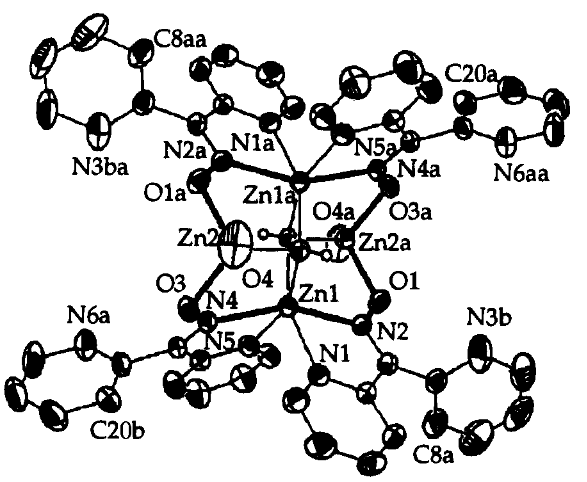

**Figure 1.** ORTEP drawing of *inv*(O)$_2$[12-MC$_{Zn^{2+}N(pko)}$-4], **1**, with thermal ellipsoids at 30% probability. The metallacrown ring is outlined in bold. Selected bond lengths (Å): Zn(1)−O(2)a = 2.071(3), Zn(1)−O(2) = 2.110(3), Zn(1)−N(2) = 2.152(4), Zn(2)−O(4) = 1.924(5), Zn(2)−O(1)a = 1.960(3), Zn(2)−O(3) = 1.966(3), Zn(2)−O(2)a = 1.980(3). Selected angles (deg): O(2)a−Zn(1)−O(2) = 78.94(12), O(2)a−Zn(1)−N(2) = 107.46(13), O(4)−Zn(2)−O(1)a = 102.9(2), O(4)−Zn(2)−O(3) = 114.5(2), O(4)−Zn(2)−O(2)a = 126.0(2), O(3)−Zn(2)−O(2)a = 103.43(12), Zn(2)a−O(2)−Zn(1) = 109.88(13), Zn(1)a−O(2)−Zn(1) = 101.05(12). Only the bound oxygen, O4, of the acetate molecule is shown here.

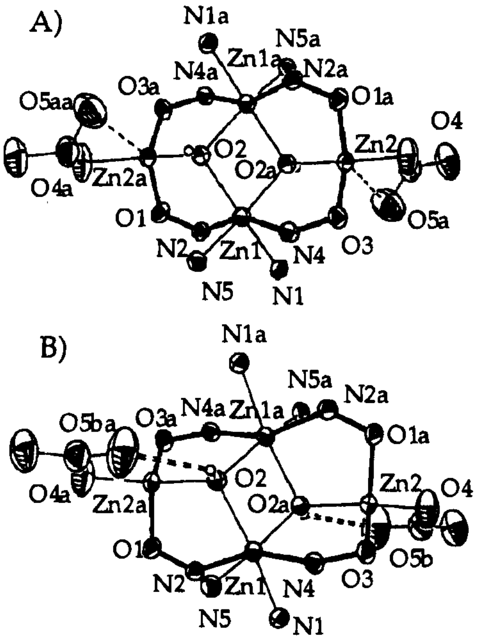

**Figure 2.** ORTEP drawings of significant atoms with one conformation (A) of the disordered acetate oxygen forming a bidentate chelate to the zinc and the second (B) showing the hydrogen bond to the $\mu_3$ bridging hydroxyl ion.

(O5) forms a weak interaction with Zn2, generating an asymmetric bidentate chelate that would be considered a class I binding acetate as described by Lippard et al.[12] This structure has an O5a−Zn2 distance of 2.57 Å and an asymmetric carboxylate stretch at 1659 cm$^{-1}$, which is consistent with the >2.5 Å distance, and an IR stretch of ~1625 cm$^{-1}$, reported for class I compounds that have a weak bonding interaction. Further support for this assignment comes from the coordination environment around the zinc which is distorted from tetrahedral geometry. The O4−Zn2−O2 angle is 126° and the O4−Zn2−O3 angle is 114°, while other angles are 101°−105°. The best description for the polyhedron is an edge-capped tetrahedron.

The hydroxyl oxygen (O2 or O2a) of complex **1** bridges to the two octahedral Zn atoms and one tetrahedral Zn atom. The coordination about the oxygen is markedly pyramidal (sum of angles about O2: 320.4°). The Zn$_4$O$_2$ core structure is similar to the Fe$_4$O$_2$ core structures[13] where the oxygens are found to be bridging $\mu_3$-hydroxyl ions instead of bridging $\mu_3$-oxo ions if the sums of the angles around the oxygen are significantly less than 360°. Careful examination of a difference Fourier map allowed placement of the hydroxyl proton at a distance of 0.81 Å, where it was held invariant. The carboxylate oxygen (O5) is disordered over two positions placed at 50% occupancy at each site. The first position, shown in Figure 2, has O5a weakly bound to Zn2 as described above. The second site, shown in Figure 2B, has some H-bonding interaction (O5b) with an H- - -O distance of 2.35 Å and a weakened Zn2−O5 (2.68 Å) distance.

This new metallacrown is unique to the 12-metallacrown-4 series in several ways. First and foremost, this metallacrown is considered "inverse" because the cationic Zn atoms, rather than anionic oxygen atoms, are oriented toward the central cavity. As a consequence, the inverse metallacrown has many other subtle structural differences from conventional metallacrowns. Usually the coordination number and environment around the metals in the metallacrown ring are uniform. In **1**, the Zn atoms are site differentiated since two metal atoms are octahedral and two are tetrahedral. Also the connectivity around the ring is different from that in other 12-metallacrown-4 compounds where the linkage is consistently N−O−M−**N**−**O**−M. Here the linkage is transposed to N−O−M−**O**−**N**−M. Metallacrowns in the past have been formed by linkage to the four heteroatoms of the ligand. In this metallacrown only three of the heteroatoms are bound, leaving one of the pyridyl nitrogens unbound. This unbound nitrogen of the pyridyl fragment of the pko ligand is disordered. The ORTEP representations in Figure 2 illustrate atoms as 30% probability ellipsoids with the disordered N/C atoms shown with the higher occupancy orientation.[14]

The architecture of the inverse metallacrown structural motif presupposes the concept of the molecular recognition of anions. Although not recognized as such at the time, an inverse 9-metallacrown-3 motif is present in several complexes involving the coordination of oximes to copper. These complexes have been isolated with bound hydroxide, perchlorate, nitrate, and sulfate anions.[15] Thus, one might anticipate differential recognition of anions by these previously described complexes. Future studies of the solution integrity and possible anion selectivity of the inverse 9-metallacrown-3 and 12-metallacrown-4 structures will be conducted.

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**Supplementary Material Available:** Tables of atomic positional parameters, selected bond lengths and angles, and isotropic and anisotropic thermal parameters (6 pages). Ordering information is given on any current masthead page.

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(14) The position of the pyridyl nitrogen could not be conclusively established, probably because there is a mixture of the two orientations in the crystal lattice. Consequently, the positions C8, N3 and C20, N6 contain pairwise contributions from carbon and nitrogen at the same site with the atomic positional parameters and anisotropic vibrational amplitudes constrained to be equal. A relative site occupancy factor was refined to account for possible unequal contributions of C and N. These factors refined to N/C ratios of 0.55(7) for N3/C8 and 0.72(5) for N6/C20.

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