The First Fused Dimer Metallacrown $Ni^{II}_2(mcpa)_2(CH_3OH)_3(H_2O)[12\text{-}MC_{Ni^{II}N(shi)_2(pko)_2}\text{-}4][12\text{-}MC_{Ni^{II}N(shi)_3(pko)}\text{-}4]$

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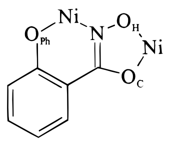
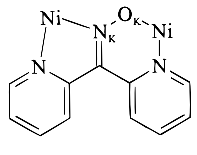
Since the discovery of synthetic crown ethers[1,2] there has been a growing interest in the phenomenon of molecular recognition. The study of crown ethers and related compounds has, in fact, given rise to a new branch of chemistry known as "host−guest" or supramolecular chemistry.[3,4] Because of the nature of the inorganic molecular recognition agents, it is possible that they could function not only as cation or anion recognition agents, but they may also be able to selectively bind ionic compounds. A series of examples of macromolecules with metal atoms, e.g., metallacrown ethers[5] or metallahelicates[6] or other structures[7−12] are now available in the literature. The development of the metallacrown class of macromolecules which shows cyclic structure generally analogous to crown ethers with transition metal ions and a nitrogen atom replacing the methylene carbons has been established in the last 8 years by Pecoraro *et al.*[13−18] while a stacking metallacrown has been reported recently.[19,20] $[9\text{-}MC_{M(ox)N(ligand)}\text{-}3]$, $[12\text{-}MC_{M(ox)N(ligand)}\text{-}4]$, and $[15\text{-}MC_{M(ox)N(ligand)}\text{-}5]$ metallacrowns with cavity size 0.35, 0.60, and 0.77 Å, respectively, and metal ions Mn^{III}, Fe^{III}, Ni^{II}, Cu^{II}, and $V^{V}O$ and a $[12\text{-}MC_{M(ox)N(ligand)}\text{-}4]$ cryptate type metallacrowns with Ga^{III} have been reported up to date.[15]

In this communication we report the synthesis and characterization of $Ni^{II}_2(mcpa)_2[Ni_4(shi)_2(pko)_2(CH_3OH)_2][Ni_4(shi)_3(pko)(CH_3OH)(H_2O)]$ (**1**) [*Hmcpa* = 2-methyl-4-chlorophenoxyacetic acid, *Hpko* = di-(2-pyridyl)ketone oxime, *H₃shi* = salicylhydroxamic acid], the first example of a fused dimer metallacrown. Compound **1** was prepared by the reaction of $NiCl_2 \cdot 6H_2O$ (2.37 g, 10 mmol), *H₃shi* (0.765 g, 5 mmol), *Hpko* (0.597 g, 3 mmol), and NaOH (0.72 g, 18 mmol) in CH_3OH (50 mL), followed by the addition of the sodium salt of *Hmcpa* (3.52 g, 16 mmol). Red/brown crystals[22] suitable for X-ray diffraction studies were obtained by slow evaporation of the mother liquid over 48 h.

The X-ray structure[23] of **1** consists of two $[12\text{-}MC_{M(ox)N(ligand)}\text{-}4]$ units[24] (Figure 1): the $Ni^{II}(mcpa)(MeOH)_2[12\text{-}MC_{Ni^{II}(shi)_2(pko)_2}\text{-}4]$ and $Ni^{II}(mcpa)(MeOH)(H_2O)[12\text{-}MC_{Ni^{II}N_{(shi)_3}(pko)}\text{-}4]$ with 1+ and 1− charge, respectively. Each unit has four ring Ni^{II} ions and one additional encapsulated Ni^{II} ion. The deprotonated salicylhydroxamic acid acts as binucleating ligand with the carbonyl and hydroxamate oxygens (O_C and O_H) bound to one nickel and the phenolate oxygen (O_{Ph}) plus imine nitrogen (N) chelating an adjacent Ni^{II}. The deprotonated ketonoxim ligand acts as binucleating ligand as well, with ketonoxim oxygen (O_K) and one pyridine-nitrogen (N) bound to one nickel and the other pyridine-nitrogen (N) plus ketonoxim nitrogen (N_K) chelating an adjacent Ni^{II}. The juxtaposed five-membered and six-membered chelates form the basis of the two metallacrown structures through a $[Ni^{II}-N-O]$ ring system that is analogous to a 12-C-4 with the



shi



pko

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(22) Analytical data for $C_{92.25}H_{89.40}Cl_2N_{14}Ni_{10}O_{32.45}$ ($[Ni_{10}(shi)_5(pko)_3(mcpa)_2(MeOH)_3(H_2O)] \cdot 3.25MeOH \cdot 1.2H_2O$): yield 70%. Found: C, 42.70; H, 3.20; N, 7.70; Ni, 14.75. Requires: C, 43.05; H, 3.45; N, 7.60; Ni, 15.15). IR, ν_{max}/cm^{-1} (KBr pellet): $\nu(C{=}N)_{shi,pko}$ 1600(vs,br); $\nu_{asym}(CO_2)_{mcpa}$ 1580(s); $\nu(C{=}O_{ph})_{shi}$ 1485(s), $\nu(C{=}O_{ox})_{shi}$ 1466(s); $\nu_{sym}(CO_2)_{mcpa}$ 1439(s); $\nu(N-O_{ox})_{shi,pko}$ 1260(vs). UV−Vis: λ(nm) (ϵ, $dm^3 \cdot mol^{-1} \cdot cm^{-1}$, *dmf* solution): 460 (2217), 345 (18 614), 310 (18 556).

(23) (a) *Crystal data* for: $C_{92.25}H_{89.40}Cl_2N_{14}Ni_{10}O_{32.45}$ ($[Ni_{10}(shi)_5(pko)_3(mcpa)_2(MeOH)_3(H_2O)] \cdot 3.25MeOH \cdot 1.2H_2O$), $M = 2571.40$, triclinic, space group $P1$, $a = 21.691(9)$ Å, $b = 16.843(8)$ Å, $c = 17.767(8)$ Å; $\alpha = 106.41(2)°$; $\beta = 100.20(1)°$, $\gamma = 99.81(2)°$, $V = 5959(5)$ Å^3; $Z = 2$; GOF = 1.074, R1 = 0.0640; wR2 = 0.1700 for 7956 refs with $I > 2\sigma(I)$. Symmetry equivalent data were averaged with $R = 0.0444$ to give 14 759 independent reflections from a total 15 177 collected. (b) Sheldrick, G. M. *SHELXS-86*: *Structure Solving Program*; University of Gottingen: Germany, 1986. (c) Sheldrick, G. M. *SHELXL-93*: *Crystal Structure Refinement*; University of Gottingen: Germany, 1993.

(24) The nomenclature used for the $[12\text{-}MC_{M(ox)N(ligand)}\text{-}4]$ cores: 12 indicates the total ring size, 4 indicates the number of oxygen donor atoms, MC specifies the metallacrown, M and ox specify the ring metal and its oxidation state [Ni(II)], N specifies the remaining nitrogen bridge, and in parenthesis are the abbreviations for the organic ligands that provide the oxygen donor atoms.

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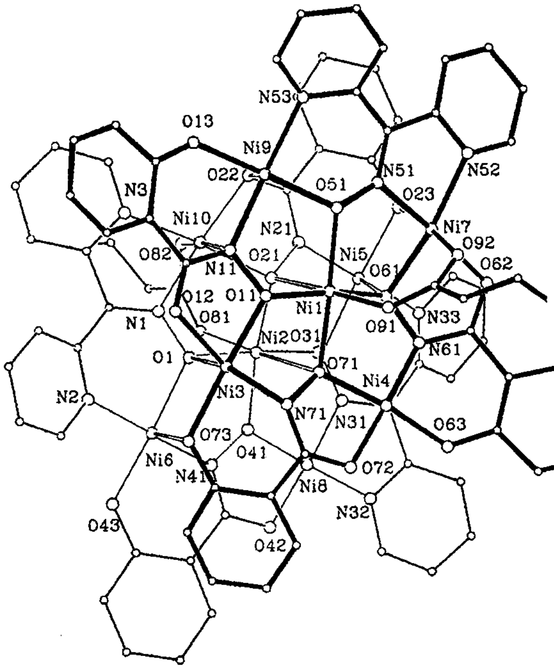

Figure 1. ORTEP diagram of the Ni^{II}_2(*mcpa*)$_2$(CH_3OH)$_3$(H_2O)[12-M-$C_{Ni^{II}N_{(shi)_2(pko)_2}}$-4][12-$MC_{Ni^{II}N_{(shi)_3(pko)}}$-4]. Only the Ni atoms and the planar binuclear moieties are labeled. The phenyl groups of the herbicide ligands and the solvent molecules(CH_3OH, H_2O) are omitted for clarity.

methylene carbons replaced with Ni^{II} and N. The average nearest-neighbor ring nickel ion separation is 4.68 and 4.70 Å, and the cavity radii are 0.65 and 0.64 Å for the anion and cation units, respectively, which allows encapsulation of a fifth nickel ion in the metallacrown core with the central Ni^{II} lying in the plane of the four oxygen ring atoms. The anionic unit is bonded with the cationic one, creating binuclear moieties [Ni(1)−O(71)−Ni(2)−O(21)], [Ni(3)−O(1)−Ni(6)−O(73)], [Ni(5)−O(61)−Ni(7)−O(23)], [Ni(9)−N(11)−Ni(10)−O(22)] with planar arrangement. The Ni^{II}(*mcpa*)(MeOH)$_2$[12-$MC_{Ni^{II}N_{(shi)_2(pko)_2}}$-4] cation with 1+ charge, has an alternating pattern of *shi*$^{3-}$ and *pko*$^{-}$ ligands as one cycles around the 12-MC-4 structure forming a neutral metallacrown ring. The Ni^{II}(*mcpa*)(MeOH)(H_2O)[12-$MC_{Ni^{II}N_{(shi)_3(pko)}}$-4] anion with three *shi*$^{3-}$ and one *pko*$^{-}$ ligands forms an anionic metallacrown ring with 2- charge and with 1− overall charge. All Ni^{II} have octahedral configuration except Ni(4) and Ni(8) with square planar configuration. The two *mcpa* carboxylato ligands are bound in a bidentate syn−syn bridging fashion to the central nickel atoms Ni(1) and Ni(2) and to the ring nickel atoms Ni(7) and Ni(10), respectively. The five Ni^{II} atoms of each metallacrown core are in the same plane with an angle between these two planes of 3.8° while the anionic metallacrown unit is shifted relative to the cationic one by about 2.00 Å. The experimental $\chi_M T$ *vs* T data taken in a 6.0 kG external field and in the temperature range 3.0−300 K show a steady decrease from 6.4 emu mol^{-1} K at 300 K to 1.7 emu mol^{-1} K at 3 K (see Supporting Information). The room temperature value of $\chi_M T$ is much lower than what would be expected for eight independent ions with spin $S = 1$ (assigning a spin value $S = 1$ to the eight six-coordinate Ni^{II} ions and considering the two four-coordinate Ni^{II} ions as diamagnetic). This indicates that at least some of the exchange interactions are strong antiferromagnetic ones. As exchange interactions in uni-core Ni^{II} metallacrowns are observed to be small ferromagnetic ones,[13] the overall antiferromagnetic behavior of **1** could result from strong intercore antiferromagnetic interactions.

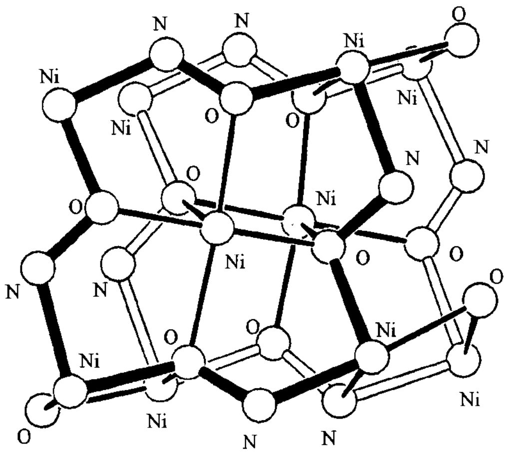

Figure 2. ORTEP diagram of Ni^{II}_2(*mcpa*)$_2$(CH_3OH)$_3$(H_2O)[12-M-$C_{Ni^{II}N_{(shi)_2(pko)2}}$-4][12-$MC_{Ni^{II}N_{(shi)_3(pko)}}$-4] (**1**) showing only the two metallacrown cores.

The geometry of the molecule would suggest the following spin-Hamiltonian:

$$\begin{aligned} H = -2J_1\vec{S}_1\{(\vec{S}_3 + S_5 + S_7 + S_9 + \vec{S}_{10}) + \\ \vec{S}_2(\vec{S}_3 + \vec{S}_5 + \vec{S}_6 + \vec{S}_{10})\} - \\ -2J_2(\vec{S}_1\vec{S}_2 + \vec{S}_3\vec{S}_6 + \vec{S}_5\vec{S}_7) - 2J_3\vec{S}_9\vec{S}_{10} \quad (1) \end{aligned}$$

assigning $\vec{S}_n$ to Ni_n (see Figure 2) and J_1 to those interactions between doubly bridged Ni^{II} with an O bridge and an O−N bridge; J_2 to those between doubly bridged Ni^{II} with two O bridges; and J_3 to one interaction with an O bridge and a N bridge. Finding the energy levels from the Hamiltonian (eq 1) is a hopeless task, so we cannot fit the experimantal data into a theoretical function. Further simplification of the Hamiltonian (eq 1) would be unrealistic. The Ni^{II} uni-core metallacrowns which have been reported[13] show weak ferromagnetically coupled systems with $J = 4.5$ cm^{-1}, $g = 2.7$, and zero-field splitting of 0.65 cm^{-1} for the {Ni^{II}-*syn*-[0,1]-(OAc)[12-$MC_{Ni^{II}N_{(nha)}}$-4]}$^{3-}$ complex. It is noticeable that the present compound shows an antiferromagnetic behavior with strong J coupling. That means it is possible a metallacrown system with similar geometrical host parameters can be regulated for its magnetic perspectives (ferromagnetic or antiferromagnetic) by choosing a uni-core or bi-core mode.

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Supporting Information Available: Tables giving magnetic susceptibility data, a plot of $\chi_M T$ *vs* T in the temperature range 3−300 K and figures of the metallacrown (20 pages). A CIF file was also deposited. Ordering and access information is given on any current masthead page.

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