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Macrocycle Formation by Proton-Template-Induced Dimerization of Complexes with (Alkoxoimino)pyridine

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Supporting Information

ABSTRACT: The existence of a strong hydrogen bond between two molecules of an (alkoxoimino)-pyridinemanganese(I) complex induces their dimerization and the formation of a metallamacrocycle. The expected intramolecular attack of the alkoxo moiety is disfavored.

The quest for useful materials has raised considerable interest toward the formation of supramolecular systems through weak interactions, such as hydrogen bonds.[1] Traditionally, it has been assumed that supramolecular organization requires a great number of weak interactions, as in the case of proteins.[2] In this context, considerable attention has been paid to the hydrogen-bonding arrangements in carboxylic acids, amides, and DNA base pairs, in an attempt to recognize patterns that would be useful for crystal engineering[3] and supramolecular assembly.[4] However, it seems that, in some cases, a small effect can play a determinant role in the formation of the final structure. The template effect of the proton in the acid-catalyzed formation of macrocycles has been recognized for over 30 years,[5] and it has been used for the rational synthesis of iminophenols,[6] macrolactams,[7] azomethines,[8] and supramolecular assemblies such as helicates,[9] catenanes,[10] and rotaxanes.[11] It has been proposed that the function of the proton as a template occurs by preorganization of the reagents through hydrogen bonding.[12]

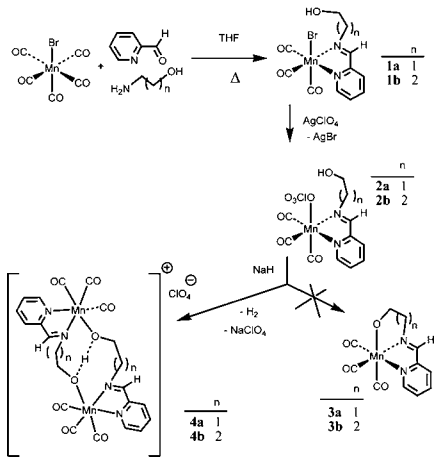
The Schiff condensation between pyridine-2-carboxaldehyde (pyca) and a functionalized amine is an attractive way to obtain iminopyridine ligands bearing a side arm derived from amino acid[13] or amino ester,[14] peptide,[15] aminophenol,[16] or ethynylaniline,[17] capable of further reactivity, or to establish hydrogen-bonding arrangements in the solid state. We present here the spontaneous formation of dimers through a process that seems to be driven by the presence of a proton.

The study of metallamacrocycles[18] and metallacrowns[19] is a very active area because of the intrinsic interest of their properties and their potential usefulness as receptors for cations and small molecules.

On the other hand, there has been increasing interest in the so-called proton complexes.[20] Within this context, the dimeric complexes described in this work can be envisaged as proton chelates and, as far as we know, they are the first examples in which a proton is coordinated by a metallamacrocycle.

The reaction of $[MnBr(CO)_5]$ with an equimolar mixture of pyca and ethanolamine produces complex $[MnBr(CO)_3\kappa^2(N,N')$-py-2-CH=$NCH_2CH_2OH]$ (**1a**; see Scheme 1), which contains an iminopyridine ligand bearing a 2-hydroxyethyl side arm, as confirmed by X-ray determination (Figure 1).

Scheme 1. Reactions Leading to the Formation of the Dimer Complexes 4a and 4b



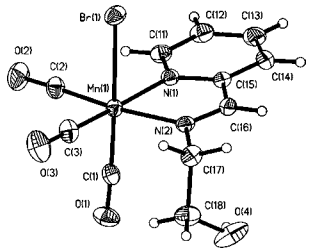


Figure 1. Molecular structure of **1a**.

The reaction of **1a** with $AgClO_4$, followed by filtration, produced a solution of the perchlorate complex **2a**. It was expected that deprotonation of the hydroxy group with sodium hydride would lead to an intramolecular attack on the manganese atom to produce a mononuclear complex, with a tridentate (alkoxoimino)pyridine **3a**. Instead, the spectroscopic features of the product in solution pointed to the formation of a dimer. Subsequent workup led to the isolation of **4a** as red crystals.

Crystal structure determination revealed that **4a** (see Figure 2) is produced by the intermolecular attack of the alkoxo group

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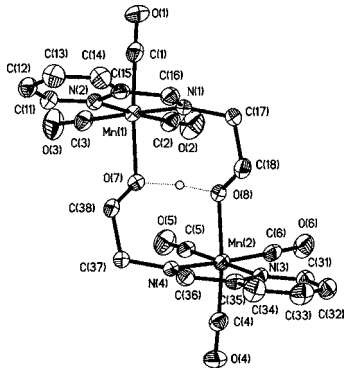

Figure 2. Molecular structure of the cation $[Mn(CO)_3\kappa^2(N,N')\kappa^1(O)$-py-2-CH=$NCH_2CH_2O\}_2H]^+$ in **4a** showing the proton bonded between the two oxygen atoms, O(7) and O(8). Relevant distances (Å) and angles (deg): O(7)···H(1) 1.268(4), O(7)···O(8) 2.414(5), H(1)···O(8) 1.135(4); O(7)···H(1)···O(8) 169.9(3).

to the manganese atom of a molecule of **2a**. Complementary coordination of the alkoxo group to the manganese atom of the first molecule produces closure of the ring, forming a 10-membered metallacycle.

Interestingly, one hydrogen atom from the hydroxy groups remains bonded to both oxygen atoms of the alkoxo ligands. The central hydrogen atom could be located in a difference map, and its position was kept fixed during the refinement. The presence of the proton is supported by the NMR experiments (see the Supporting Information).

In **4a**, the distance O(7)−O(8) of 2.419 Å is shorter than 2.446 Å found in the crown ether complex of $HPCl_6$ reported by Tessier et al,[21] this being consistent with a strong O−H−O hydrogen bond.[22]

Because of sp^2 hybridization of the imine nitrogen, the α-carbon atom of the side chain, C(17) in Figure 1, must be coplanar with the iminopyridine system. This geometric constrain to the side chain does not permit an intramolecular attack to the manganese atom to give mononuclear alkoxo derivative **3a**. In order to prove that the formation of the dimer is driven by the template effect of the proton and is not due to geometrical restrictions, the same sequence of reactions was performed starting from propanolamine (i.e., with an additional carbon atom in the chain).

The resulting product is again a dimer, **4b** (see Scheme 1), instead of the monomer **3b**, which would result from the intramolecular attack on manganese. This is confirmed by spectroscopic data and X-ray structure determination. The structure of **4b** contains two crystallographically independent, but chemically equivalent, molecules. It can be seen in Figure 3 that the structure of **4b** reproduces the most significant features of **4a**, except for the additional carbon atom in the chain. The distances between the oxygen atoms of the alkoxo chains involved in the bonding with the proton are now 2.448(5) and 2.470(5) Å, only slightly longer than the values found for **4a** and close to the distances observed in the crystal of the crown ether complex of $HPCl_6$.

The ^1H NMR spectra of **4a** and **4b** show the usual signals of an iminopyridine and a set of complex multiplets for the diasterotopic aliphatic protons. The assignment of all of the signals has been done with the help of $^1H-^1H$ COSY, $^1H-^{13}C$ HSQC, and $^1H-^1H$ NOE experiments, which are collected in the Supporting Information.

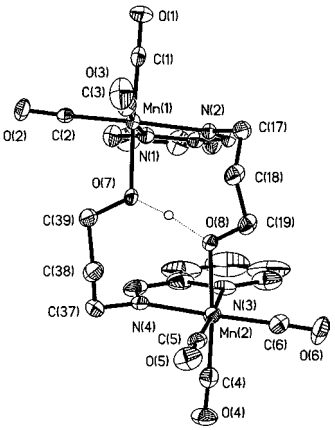

Figure 3. Molecular structure of the cation $[Mn(CO)_3\kappa^2(N,N')\kappa^1(O)$-py-2-CH=$NCH_2CH_2CH_2O\}_2H]^+$ in **4b**. Even with an extra carbon atom, C(19), in the alkoxo chain, it still adopts a dimeric structure stabilized by the proton bonded to O(7) and O(8) (see the text for an explanation). Only one of the two molecules of the asymmetric unit is shown. The geometrical parameters of the other molecule are not significantly different. Relevant distances (Å) and angles (deg) for molecule 1: O(7)···H(1) 1.119(4), O(7)···O(8) 2.448(5), H(1)···O(8) 1.335(4); O(7)···H(1)···O(8) 172.0(2). Relevant distances (Å) and angles (deg) for molecule 2: O(57)···H(2) 1.077(4), O(57)···O(58) 2.470(5), H(2)···O(58) 1.406(4); O(57)···H(2)···O(58) 168.1(3).

The dimeric structures of **4a** and **4b** are maintained in solution and, accordingly, the proton bonded between the two oxygen atoms appears at very low field (more than δ 12 ppm), corresponding to a strong hydrogen bond. The spectrum shows only one set of signals for the iminopyridine ligands, which behave as equivalent because of the existence of an effective C_2 axis of symmetry. The existence of a nuclear Overhauser effect (NOE) between the pyridinic proton H^6 in one moiety and the α-methylenic protons of the other moiety confirms that the structure is dimeric in solution (see the Supporting Information).

Several attempts to remove the central proton proved the robustness of the O···H···O arrangement: when a large excess of NaH was added to a solution of **4**, the IR spectrum showed bands at frequencies significantly lower than those of a dimer cation [cf. 2019 and 1921 cm^{-1} versus 2037 and 1932 cm^{-1} (br) for **4a**] that could be attributable to the neutral deprotonated species. However, despite repeated attempts, it was not possible to isolate such neutral species. It seems that it is protonated again very easily by trace water or by scavenging protons from the solvent. In all cases, the cationic dimers were recovered, although with some decomposition. This is again proof of the stability of the dimer having the central proton bonded to the oxygen atoms. It is worth noticing that the complex with crown ether mentioned above has to be done in superacid conditions, while the dimers **4** are produced after partial deprotonation with NaH. Moreover, the fully deprotonated, neutral species behaves as a very strong base, in a proton sponge fashion.

In conclusion, the presence of a proton strongly bonded between the two oxygen atoms of the alkoxo ligands helps to keep the metals together, thus serving as a template to form a 10- or 12-membered dimetallamacrocycle. This, in turns, acts as a strongly basic macrocyclic ligand toward the proton

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■ ASSOCIATED CONTENT

Supporting Information

Experimental section, ^{1}H, HSQC, COSY, NOESY, and EXSY NMR spectra of **4b**, and crystallographic data (also in CIF format) for **1a** (CCDC 839711), **4a** (CCDC 839712), and **4b** (CCDC 839713). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ DEDICATION

Dedicated to the memory of Prof. F. Gordon A. Stone.

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