The First Case of Local *cis* versus *trans* Coordination as the Controlling Factor for the Overall Structure in Dinuclear Assemblies

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The preparation and structure of two dinuclear assemblies $[M_2(HL)_2(py)_4]$ (M^{II} = Mn, Ni) with the phenol bis-β-diketone H_3L are presented. The octahedral N_2O_4 coordination environments around the metals are in *cis* and *trans* configuration for Mn and Ni, respectively, leading to structurally different assemblies. These results represent the first example where the overall structure of a complicated coordination architecture is controlled by the local stereochemistry imposed at the metal ions.

Introduction

In the creation of complicated coordination supramolecular assemblies, the information leading to the final architecture is contained in the structural and electronic properties of the ligands as well as in the specific requirements of the transition metals.[1] This is best illustrated by cases where very different structures are obtained when all but one of the parameters of the system are maintained constant.[2−7] For example, a ligand has been reported whose molecular information is expressed in form of either a circular or a cross-shaped dodecanuclear assembly depending on the set of metals that is allowed to react with it, and this is dictated by the coordination geometry imposed by them.[6] In a different example, small differences in the spacer between donor sites in polynucleating ligands determine whether a grid-like complex or a helicate is obtained from the same transition metal.[3,4] The understanding and control of the factors that lead to each particular architecture are paramount to bring about the ambitious potential technological applications of this field. We report here a unique example where the preferred *cis*/*trans* stereochemistry at the metal centers determines the overall architecture of the dinuclear complexes that they form with the same ligand.

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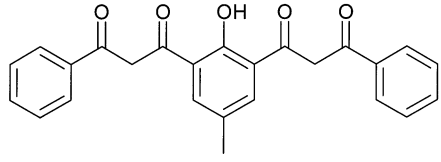
Supporting information for this article is available on the WWW under http://www.eurjic.com or from the author.

Results and Discussion

The ligand H_3L[8] has been prepared recently[9] (Scheme 1) and its coordination properties with a variety of transition metals are just starting to be explored. The versatility provided by the presence of a phenol and two β-diketone units in this molecule has already afforded a diversity of supramolecular architectures.[10,11]



Scheme 1. H_3L in its ketonic form and *syn-syn* conformation

The X-ray structure of H_3L has been determined[12] using single crystals obtained from a solution in acetone and it is presented in this report (Figure 1). Consistent with the solution ^1H NMR spectroscopic data, the Fourier maps of this diffraction experiment also revealed the β-diketone groups to lie completely in their enolic form. In one of these units, the acidic H is found to be disordered between the oxygen atoms. One apparent and striking feature of this essentially flat molecular structure is the *anti-syn* conformation displayed by the β-diketone units with respect to the phenol group. No intermolecular hydrogen bonding or π-π contacts have been identified in the crystal lattice, suggesting this conformation to be the result of intramolecular

interactions, as supported by molecular modeling calculations performed on H_3L.[13] Presumably, this nuclear topology allows for the most favorable interactions between the numerous local electric dipoles present in this molecule.

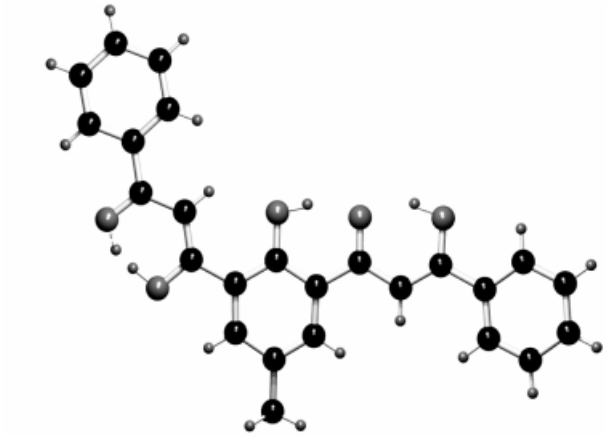


Figure 1. Pov-ray drawing of the X-ray structure of H_3L displaying its enolic form and *anti-syn* conformation

The reaction of equimolar amounts of H_3L and $Mn(OAc)_2$ or $Ni(OAc)_2$ in pyridine produced high yields of orange or green crystals of $[M_2(HL)_2(py)_4]$ (M = Mn, **1**; Ni, **2**) upon addition of Et_2O (**1**) or after layering the reaction mixture with toluene (**2**). Both types of crystals were suitable for X-ray crystallography and analyzed satisfactorily.[14]

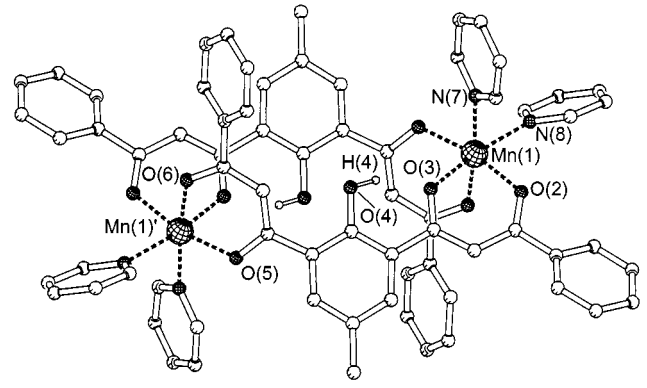


Figure 2. Platon drawing of $[Mn_2(HL)_2(py)_4]$ (**1**); selected bond lengths (Å): Mn(1)−O(2) 2.1522(15), Mn(1)−O(3) 2.1651(14), Mn(1)′−O(5) 2.1557(13), Mn(1)′−O(6) 2.1337(14), Mn(1)−N(7) 2.2415(17), Mn(1)−N(8) 2.2631(16), Mn(1)···Mn(1)′ 9.3018(13), O(3)···O(4) 2.4753(19)

The structure of **1**[12] (Figure 2) consists of a centrosymmetric complex of two Mn^{II} ions, chelated and bridged by two crystallographically equivalent HL^{2-} ligands. Interestingly, the ligands in this complex lie in the same conformation as that of the free ligand in the solid state, although much more removed from planarity [the angle between the idealized planes containing both β-diketonate groups is 40.74(9)° in **1** and 7.53(11)° in H_3L]. In addition, the presence of intramolecular hydrogen bonding between O(3) and O(4) is revealed in this structure [O(3)···O(4) = 2.4753(19) Å], where H(4) has been refined. The metals in this assembly are separated by a distance of 9.3018(13) Å, and are accommodated in a slightly distorted octahedral geometry. An oxidation state of 2+ has been assigned to Mn based on charge considerations, and is consistent with the magnetic properties of **1** (vide infra).

X-ray diffraction analysis performed on crystals of **2**[12] showed this compound to be an assembly of two Ni^{II} centers bridged by two HL^{2-} chelating ligands, with the coordination around each metal completed by two pyridine ligands (Figure 3). A crystallographic center of symmetry is also present in the middle of the molecule in this case. In contrast to **1**, however, the polynucleating ligands in this complex are found in the *syn-syn* conformation. This leads to an overall architecture that is completely different to that in **1** despite the fact that these two compounds share the same formulation, with the exception of the nature of the metals. A closer examination of the structure of **2** allows one to conclude that this major structural change is the consequence of the local stereochemistry at the metal centers. The coordination geometry around Ni is octahedral with a slight tetragonal elongation. Comparing **1** with **2**, it can be seen that the N_2O_4 coordination sphere around Ni^{II} is in a *trans* configuration, as opposed to the *cis* stereochemistry with Mn^{II}. The HL^{2-} ligand in **2** is not completely planar [the β-diketonate planes form an angle of 46.61(7)°] and also shows the same [O−H···O] interaction [O(3)···O(4) = 2.5047(15) Å] as in **1**. Furthermore, the conformational disparity between **1** and **2** leads to a markedly shorter metal-metal distance in the latter complex, the Ni···Ni distance being 7.9210(8) Å. The same arguments as for **1** are used for the assumption about the oxidation state of Ni in **2**. Crystals of the related complex $[Ni_2(HL)_2(py)_2(THF)_2]$ were also analyzed and show the same structural features as **2**. Details of this determination are included in the Supporting Information (see footnote on the first page of this article).

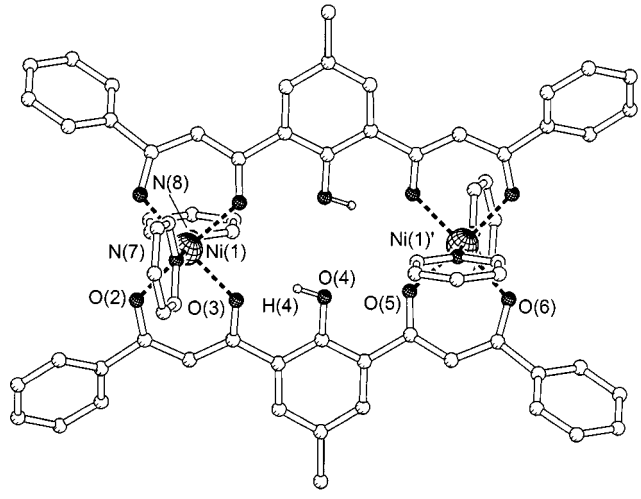


Figure 3. Platon drawing of $[Ni_2(HL)_2(py)_4]$ (**2**); selected bond lengths (Å): Ni(1)−O(2) 2.0297(10), Ni(1)−O(3) 2.0241(10), Ni(1)′−O(5) 2.0092(10), Ni(1)′−O(6) 2.0295(10), Ni(1)−N(7) 2.1067(13), Ni(1)−N(8) 2.1136(13), Ni(1)···Ni(1)′ 7.9210(8), O(3)−O(4) 2.5047(15)

The structural difference between **1** and **2** is not mirrored in their magnetic properties, as shown by bulk magnetization measurements in the 2−300 K temperature range at a constant field of 1 kG. In both cases, the magnetic susceptibility data could be fitted with a model that considers two noninteracting M^{II} centers, yielding ionic *g* values of 2.01 and 2.10 for Mn^{II} and Ni^{II}, respectively.

The local *trans* configuration preferred in complex **2** is ascribed to the larger crystal field stabilization energy that results from this donor distribution, one that is observed in the vast majority of Ni^{II} complexes with an equivalent set of ligands.[15] This thermodynamic argument does not apply to high-spin Mn^{II} (d^5). Therefore, the *cis* stereochemistry is observed at the metal ions in **1**, most probably because it is the one that allows for the most stable conformation of the polynucleating ligand. To the best of our knowledge, this is the first example where the overall structure of a polynuclear assembly is determined solely by the difference in the local *cis*/*trans* configuration of the metals. A related precedent exists where a dinucleating ligand delivers either a helicate or a mesocate, depending on the metal used, the structure of the assembly being dictated by the chirality at the coordination centers.[16] Additional examples of the simple principle manifested experimentally for the first time in the present work are currently under investigation with different metals. A thorough study will be published in due course.

Acknowledgments

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[12] Crystal structure determinations were carried out at 150 K. Data were measured on a Nonius KappaCCD diffractometer with a rotating anode (Mo-K_α radiation, graphite monochromator, $\lambda = 0.71073$ Å). Structures were solved by direct methods (SHELXS-86) and refined on F^2 with SHELXL-97. The coordinates of the hydroxyl hydrogen atoms were refined; other hydrogens were included in the refinement at calculated positions riding on their carrier atoms. No absorption correction was applied.
Data for $\mathbf{H_3L}$: $C_{25}H_{20}O_5$, $M_r = 400.41$, yellow, needle-shaped crystal (0.05 × 0.12 × 0.40 mm), orthorhombic, space group $Pna2_1$ (no. 33) with $a = 7.625(2)$, $b = 22.540(6)$, $c = 11.193(2)$, Å $V = 1923.7(8)$ Å^3, $Z = 4$, $D_c = 1.383$ g cm^{-3}, μ(Mo-K_α) = 0.096 mm^{-1}, 14561 reflections measured ($1.6° < \theta < 27.47°$), 2317 independent (Friedel pairs were averaged), $R_{int} = 0.0657$. A hydrogen atom was found to be disordered between O5 and O6; the coordinates of both positions were refined. The occupancy of the major component refined to 0.59(11). 285 parameters were refined, $wR2 = 0.0873$, $R1 = 0.0383$ [for 1796 reflections with $F_o > 4\sigma(F_o)$] $S = 1.020$, $-0.25 < \Delta\rho < 0.15$ e Å^{-3}.
Data for **1**: $C_{70}H_{56}Mn_2N_4O_{10}\cdot 5C_5H_5N$, $M_r = 1618.62$, orange, needle-shaped crystal (0.1 × 0.1 × 0.3 mm), monoclinic, space group $C2/c$ (no. 15) with $a = 25.215(3)$, $b = 15.166(2)$, $c = 21.295(2)$ Å, $\beta = 91.455(9)°$, $V = 8140.8(16)$ Å^3, $Z = 4$, $D_c = 1.321$ g cm^{-3}, μ(Mo-K_α) = 0.398 mm^{-1}, 72705 reflections measured ($1.6° < \theta < 25.21°$), 7323 independent, $R_{int} = 0.0761$. Electron density in a disordered solvent area containing 2.5 unique pyridine molecules was taken into account in the refinement via PLATON/SQUEEZE. Where relevant, the data cited above are given with the contribution of this disordered solvent. 393 parameters were refined, $wR2 = 0.1100$, $R1 = 0.0423$ [for 5551 reflections with $F_o > 4\sigma(F_o)$] $S = 1.066$, $-0.28 < \Delta\rho < 0.28$ e Å^{-3}.
Data for **2**: $C_{70}H_{56}N_4Ni_2O_{10}\cdot 2C_7H_8\cdot 2C_5H_5N$, $M_r = 1574.04$, light green, block-shaped crystal (0.15 × 0.20 × 0.30 mm), triclinic, space group $P\bar{1}$ (no. 2) with $a = 11.0980(10)$, $b = 12.0326(12)$, $c = 15.5168(15)$ Å, $\alpha = 88.854(10)°$, $\beta = 78.382(10)°$, $\gamma = 79.478(10)°$, $V = 1995.2(3)$ Å^3, $Z = 1$, $D_c = 1.309$ g cm^{-3}, μ(Mo-K_α) = 0.537 mm^{-1}, 58280 reflections measured ($1.6° < \theta < 27.49°$), 9138 independent, $R_{int} = 0.0414$, 510 parameters, $wR2 = 0.0840$, $R1 = 0.0321$ [for 7934 reflections with $F_o > 4\sigma(F_o)$] $S = 1.044$, $-0.49 < \Delta\rho < 0.53$ e Å^{-3}.
CCDC-174297−174300 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].
[13] This was done by molecular mechanics (MMF) and semi-empirical (PM3) methods as executed with the SPARTAN package (SPARTAN 5.1, Wavefunction, Inc., 18401 Von Karman Ave., Ste. 370, Irvine, CA 92612 U.S.A).
[14] **1**: $C_{70}H_{56}Mn_2N_4O_{10}$ (1223.1): calcd. C 68.74, H 4.61, N 4.58; found C 68.50, H 4.57, N 4.70. **2**·0.3py: $C_{71.5}H_{57.5}N_{4.3}Ni_2O_{10}$ (1254.33): calcd. C 68.58, H 4.47, N 4.81; found C 68.11, H 4.94, N 4.68.
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