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# Dissymmetric binucleating ligands containing a salophen and bisoxamato cavities

Benedikt Lassalle-Kaiser, Régis Guillot and Ally Aukauloo*

*Institut de Chimie Moléculaire et des Matériaux d'Orsay, UMR8182 CNRS, Bât. 420 Université Paris-Sud 91405 Orsay, France*

**Abstract**—The synthesis of a dissymmetric biscompartmental ligand holding a salophenic and a bisoxamate coordinating cavities is described. The electrochemical behaviour and X-ray crystallographic data of the dinuclear nickel(II) complex are reported.
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The primary interest of chemists in multimetallic systems is to achieve reactivity patterns and physical properties that could not be attained with the monometallic complexes. In this line of thought, several families of binucleating ligands together with their homo and heterobimetallic complexes have been prepared.[1–5] Although to date only a few bimetallic complexes were found to possess unique chemical reactivities and physical properties.[2] Recently, a new class of metal-organic framework (MOF) has been designed with the target to reproduce a zeolitic-like environment around a molecular catalytic site.[6–8] These materials provide unique properties such as control of the substrate size, better selectivity, enhancement of catalytic activity, as well as easy recovery of the catalyst. Moreover, the extended molecular architecture incorporating the catalyst avoids the deleterious encounters of active forms of the catalyst. A common synthetic route leading to the MOF embedding a catalyst is the introduction of a binding site on the periphery of a molecular catalyst skeleton. Coordination scheme to an exogenous metal ion specifically drive the formation of extended arrays. Pyridine and carboxylic functionalities have been most widely used to now.

With the aim to deploy new molecular blocks in the development of this emerging field we have been inter-

ested in the design of a molecular unit bearing at the same time a connector site and a putative catalytic core. For the connector unit, we took profit from a well-established coordination chemistry for molecular magnetism,[9] developed in our laboratory. In this field, paramagnetic metal complexes are used as ligands towards other metal ions to generate a controlled network of metal ions. The bisoxamato metal derivatives have been intensively used as a building block. The $[Cu(OPBA)]^{2-}$ (OPBA = $o$-phenylene bisoxamate) complex acts as the archetypal molecular unit to generate infinite 1D, 2D and 3D networks through binding of the external oxygen atoms of the oxamate fragments to a metal ion.
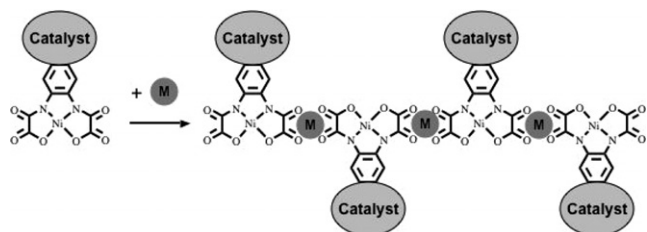
In this project, our target proligand cumulates at the same time a bisoxamate unit serving as the structural template and a salophen cavity representing the putative catalytic site. We describe herein the synthesis (Scheme 2) and characterisation of the first representative heterodinuclear nickel(II) complex. The central core holding both cavities is the tetraaminobenzene derivative. This motif has been used to prepare symmetric tetraoxamate,[5] bis-salophen[10] and other symmetric biscompartmental ligands.[3] However, no synthesis of dissymmetric ligand has been attempted. The key molecule leading to the synthesis of this dissymmetric biscompartmental ligand is the 1,2-dinitro-4,5-diaminobenzene (**1**), which was prepared following literature procedure.[11] After reaction with ethyloxalyl chloride in tetrahydrofuran, the diethyl ester of 1,2-dinitro-$N,N'$-4,5 dioxamic benzene was isolated in an almost quantitative yield. The reduction of the nitro groups was realised in presence

of supported Palladium/charcoal catalyst (10%) under hydrogen pressure in good yield. At this point, instead of preparing the salophen cavity to give the free ligand, we followed the 'template synthesis' approach by running the condensation reaction with salicylaldehyde in presence of a divalent metal ion. For instance, Ni(II) leads to a quantitative yield of compound **4**, where the salophenic coordinating hole is occupied by the Ni(II) ion. Therefore, this synthetic route already sets up the basis for sequential metallation of both coordinating cavities. Metallation of the bisoxamate cavity was then realised by treating **4** with four equivalents of base to deprotonate the amide groups and saponify the ester groups, followed by slow addition of one equivalent of the nickel salt (Nickel(II) nitrate·6H$_2$O). The tetraphenylphosphonium derivative of Ni$_2$ complex (**5**) was easily obtained by metathesis.

The choice of inserting Ni(II) ion in both cavities was guided by the diamagnetic nature of the latter in a square planar environment. Therefore the metallation steps (iii and iv) in Scheme 1 were easily monitored by proton NMR. The spectra of dinuclear complex **5** resembles those of the mononuclear counterpart except that no signals corresponding to the amido protons are observed in both cases. An upfield chemical shift is observed for the methine protons and the aromatic protons of the central benzenic ring by ca. 0.6 and 0.1 ppm, respectively. This results probably from the different electronic distributions of electronic density within the dianionic dinuclear complexes when compared to the neutral mononuclear ones. Cyclic voltammograms of [**5** (PPh$_4$)$_2$] shows a first anodic process at $E_{1/2} = 0.44$ V vs SCE ($\Delta E_p = 90$ mV). This redox behaviour is very similar to the one observed for the 4,5-hydrogen substituted mononuclear oxamate species.[12] However, it is shifted to more anodic potential by 400 mV compared to the previously reported first oxidation process of the bisoxamato nickel compound.[5] This fact suggests that the presence of the two imino groups on the opposite side of the bisoxamate cavity relieve the charge density on the central aromatic ring and shifts the locus of the oxidation from the ligand to the metal ion in the tetraanionic cavity. Interestingly, the presence of the nickel(II) ion in the salophen cavity seems to have a negligible influence on the redox potential of the nickel ion in the bisoxamato cavity. Apparently the two metal ions behave independently from each other in this molecular scaffold, at least in the case of the dinuclear nickel(II) complex.

The X-ray crystallographic data for compound **5** were obtained and an ORTEP view with atom numbering is shown in Figure 1. As expected, the coordination environment of each nickel atom is essentially square-planar. The main metric data are given in Table 1. The average Ni–N and Ni–O bond lengths are identical to those found for the monomeric nickel(II) complexes for the bisoxamato[5] cavity, as well as the salophen[13] cavity. The shorter bond lengths for the Ni–N distance for the deprotonated amide functions compared to the imine functions are indicative of a stronger interaction



Scheme 1. 'Complex as ligand' strategy applied to the construct of coordination networks.



Scheme 2. Synthetic route for the preparation of **5**: (i) ClCOCOEt/THF (ii) H$_2$/40 bars/Pd (iii) Ni(NO$_3$)$_2$·6H$_2$O/salicylaldehyde (iv) NaOH/Ni(NO$_3$)$_2$·6H$_2$O.
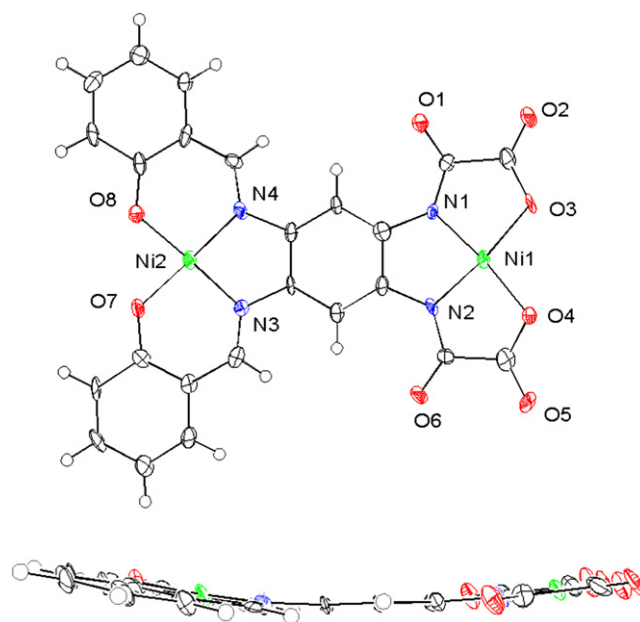


Figure 1. ORTEP drawing of complex **5**. Top view (top) and side view (bottom). Ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

**Table 1.** Selected bond lengths and angles for [**5** (PPh$_4$)$_2$]

| Oxamate | | Salophen | |
|---|---|---|---|
| Ni$_1$–N$_1$ | 1.819 Å | Ni$_2$–N$_3$ | 1.862 Å |
| Ni$_1$–N$_2$ | 1.821 Å | Ni$_2$–N$_4$ | 1.844 Å |
| Ni$_1$–O$_3$ | 1.893 Å | Ni$_2$–O$_7$ | 1.839 Å |
| Ni$_1$–O$_4$ | 1.878 Å | Ni$_2$–O$_8$ | 1.830 Å |
| N$_1$–Ni$_1$–N$_2$ | 85.78° | N$_3$–Ni$_2$–N$_4$ | 86.84° |
| N$_1$–Ni$_1$–O$_3$ | 86.78° | N$_3$–Ni$_2$–O$_8$ | 94.88° |
| N$_2$–Ni$_1$–O$_4$ | 86.56° | N$_4$–Ni$_2$–O$_7$ | 94.56° |
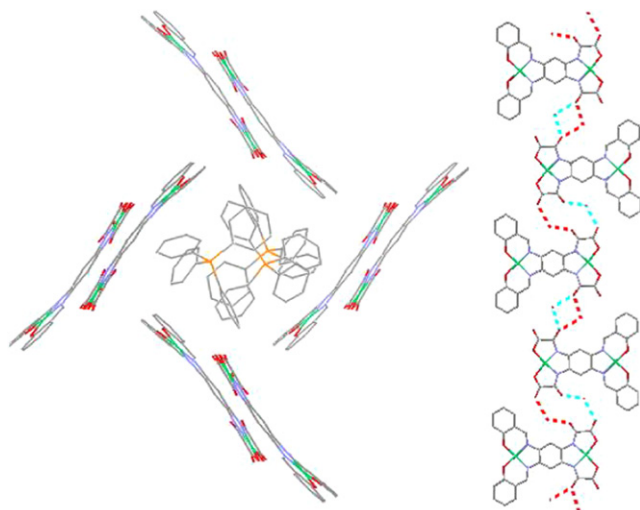


**Figure 2.** The square channel with the counter-ion hosts (left) and the linear supramolecular network (right) observed in the crystal structure of [**5** (PPh$_4$)$_2$].

in the case of the anionic nitrogen atoms. While the difference in the Ni–O distances is attributable to the steric requirements of the three five membered metallacycles in the case of the bisoxamato coordinating site compared to the less strain alternating six–five–six-membered rings for the salophen cavity. The intermetallic distance is 6.34 Å and is within the range found in dinuclear complexes separated by a benzenic ring.[4,5,3] The entire ligand skeleton is nearly planar [maximum deviation from the mean molecular plane of 0.264(2) Å for O(5)]. The observed C–C *intra* ring benzene distances are almost equivalent, and are intermediate between those of single and double bonds (average 1.40 Å), whereas the C–N bond distances from the benzene ring to the amide nitrogens are characteristic of single bonds (average 1.42 Å), thereby reflecting complete π-delocalisation mainly within the benzene ring.

An interesting feature of the solid state structure of [**5** (PPh$_4$)$_2$] is that the crystal lattice is dominated by a hydrogen bonding network running through the oxamate fragments and the intercalated water molecules of crystallisation. As indicated in Figure 2, two contiguous dianionic bricks following the *z*-axis disposed the salophen cavities in an opposite configuration probably

for minimising steric constraints. The oxamate fragments of two molecules are bridged through one or two water molecules. It is worthnoticing that the hydrogen bonding pattern leads to an interdigitation of the dianionic motifs. The linear networks thus formed are set perpendicular to each other, generating a channel of about 12.5 Å of side. The tetraphenyl phosphonium counter-ions fill in the void created by the formation of these channels.

As we mentioned above, the bisoxamate cavity will serve as the template to initiate the infinite network of the dissymmetric unit. Therefore, one can expect that the replacement of the water molecules between the external oxygen atoms of the oxamate ligands by a metal dication will lead to the formation of an extended molecular network. Also, as benchwork, heterodinuclear complexes with metals ions such as cobalt, manganese, and iron in the salophen cavity are underway.

## Supplementary data

## References and notes

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