Inorganic Chemistry
Communication
pubs.acs.org/IC

Direct C−N Coupling in an in Situ Ligand Transformation and the Self-Assembly of a Tetrametallic [Ni^{II}_4] Staircase

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Supporting Information

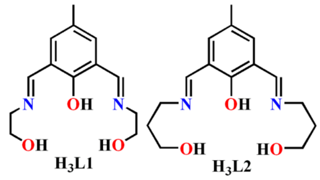
ABSTRACT: A [Ni^{II}_4] staircase complex was serendipitously prepared from the reaction of the binucleating Schiff base proligand 2,6-bis[[(3-hydroxypropyl)imino]methyl]-4-methylphenol (H_3L2) and 3,5-dimethylpyrazole (Me_2pzH) with nickel(II) nitrate in a reaction at room temperature, initially aimed to yield a dinuclear complex. From a room temperature metal ion/ligand reaction, the proligand H_3L2 in situ transformed to modified forms $HL3^{2-}$ and $HL4^{2-}$, allowing the [Ni_4] formation. Variable-temperature magnetic behavior of a [Ni_4] complex reveals antiferromagnetic interactions with stabilization of a diamagnetic ground state ($S_T = 0$).

The advancement of new synthetic strategies to self-assemble high-nuclearity transition-metal complexes from simple ligand precursors and transition-metal salts has enriched the research for coordination cluster synthesis.[1] From paramagnetic metal ions, the development of such molecular spin clusters thus has become one of the principal topics in molecular synthesis.[2] In this regard, serendipity plays a role of choice and is widely recognized as a possible path to preparing high-nuclearity coordination compounds.[3] Although it is not possible to dictate the outcome of any such reaction of a metal ion and a ligand in solution, one can take control of the reaction protocol once the serendipitous self-assembly product has been identified. In situ metal ion/ligand reactions have been extensively used for ligand transformation, elucidation of reaction mechanisms, and one-pot synthesis of unique coordination complexes that are strictly inaccessible otherwise.[4] Quite often such methods provide carbon−carbon coupling, hydroxylation of aromatic rings, cycloaddition of organic nitriles with azide and ammonia, transformation of inorganic and organic sulfur, and decarboxylation of aromatic carboxylates.[5] In contrast, in situ one-pot metal ion/proligand reactions in air and under mild conditions have not been systematically explored to obtain hitherto unknown organic ligands that are inaccessible following standard organic reaction protocol.

Serendipitous synthesis often sees beautiful and novel structural types beyond the imagination of a synthetic chemist. Variation of ligand donor groups, their bridging ability, and flexibility in coordination arms is crucial to controlling the molecular aggregates.

In search of unique metal salt/ligand reactions, recently we have introduced 2,6-bis[[(2-hydroxyethyl)imino]methyl]-4-methylphenol (H_3L1; Scheme 1) and 2,6-bis[[(3-hydroxypropyl)imino]methyl]-4-methylphenol (H_3L2; Schemes 1 and S1 in the Supporting Information, SI) ligands to construct $\{Cd_2\}$,[6] $\{Zn_3\}$,[7] $\{Ni_4\}$,[8] $\{Co_4\}$,[9] $\{Cu_4\}$,[10] $\{Ni_5\}$,[8] $\{Cu_5\}$,[11] $\{Ni_6\}$,[12] $\{Ni_7\}$,[13] $\{Ni_8\}$,[14] and $\{Cu_{12}\}$[15] aggregates showing characteristic fluorescent and magnetic behaviors. Interesting results have been documented by other groups as well, consisting of $\{Cu_4\}$,[16] $\{Cu_8\}$,[17] $\{Cu_{18}\}$[18] and $\{Mn_{12}Cu_8\}$[19] assemblies.

Scheme 1. H_3L1 and H_3L2

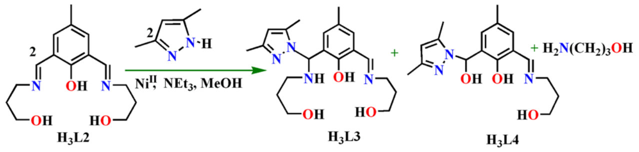


Herein, we present a unique example of serendipity in the form of the first example of a polynuclear metal complex, namely, the $[Ni_4(\mu\text{-}HL3)_2(\mu_3\text{-}HL4)_2]\cdot 2MeOH\cdot 2H_2O$ complex, comprising two hitherto unknown and transformed forms of H_3L2 (Schemes 2 and S2 in the SI), in which the initially employed ligand is absent. During the reaction plan, 3,5-dimethylpyrazole (Me_2pzH) in a basic medium was chosen to introduce Me_2pz^- as an exogenous bridging group between the two metal ions. To this end, at room temperature we reacted $Ni(NO_3)_2\cdot 6H_2O$ with H_3L2, Me_2pzH, and NEt_3 in methanol (MeOH) to obtain a green solution of pH 5.7. If the solution remained undisturbed, bright-

Received: February 19, 2015
Published: May 18, 2015

DOI: 10.1021/acs.inorgchem.5b00411
Inorg. Chem. 2015, 54, 5136−5138

Scheme 2. Formation of H_3L3 and H_3L4 from H_3L2



green X-ray-quality single crystals of **1** in 68% yield are obtained after 14 days, as described in eq S1 in the SI.

Complex **1** crystallizes in the monoclinic space group $P2_1/c$. X-ray analysis[20] revealed that the asymmetric unit comprises two Ni ions, one $HL3^{2-}$, and one $HL4^{2-}$ (Figure 1). Two Ni ions are bridged by two central phenoxido (PhO^-) groups of ligands with a Ni···Ni separation of 3.231 Å. Two such dimeric parts in **1** are related by a crystallographic inversion center passing through the midpoint of the Ni2···Ni2* axis. The dianionic $HL3^{2-}$ is generated in solution through activation of the C═N bond followed by nucleophilic attack of Me_2pz^- in the presence of NEt_3 for a C−N bond-forming reaction under the control of coordinated Ni^{II} ions (Scheme 2).

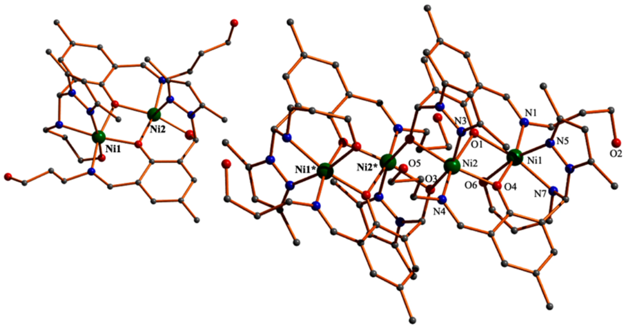


Figure 1. Asymmetric unit of **1** (left) and the $[Ni_4]$ staircase assembly with partial atom labeling (right). Symmetry code: (*) $-x, -y, -z$. Color code: Ni, green; O, red; N, blue; C, black.

The $HL3^{2-}$ ligand anion thus formed bridges two Ni^{II} ions within the tetranuclear assembly through the deprotonated phenol groups by adopting the μ-η^1:η^2:η^1 coordination mode (Scheme S2 in the SI). The other inactivated imine unit bearing an alcohol arm remains dangling. Similar transformation of bound $HL2^{2-}$ followed by alcohol arm hydrolysis results in dianionic $HL4^{2-}$, which bridges three Ni^{II} ions in μ_3-η^2:η^2:η^1 coordination mode with one pendant alcohol arm (Scheme S2 in the SI). The hydrolysis results in an unusual pyrazolyl-grafted alcohol arm at one side of $HL4^{2-}$ to connect two dinickel units in a zigzag structure having a Ni2···Ni2* separation of 3.233 Å (Figures S1−S3 in the SI). The alkoxido bridge is asymmetric toward Ni2 and Ni2* with one short (2.078 Å) and one long (2.160 Å) Ni−O bonds. The geometry around Ni1 and Ni2 is best described as distorted octahedral because bond angles in the cis and trans orientations range from 77 to 100° and from 159 to 168°. The Ni1 center coordinates to the O4, O6, N5, and N7 atoms of $HL3^{2-}$ and the O1 and N1 atoms of $HL4^{2-}$, while the O4 and N4 atoms of $HL3^{2-}$ and the O1, O3, O3*, and N3 atoms of $HL4^{2-}$ bind to the Ni2 center. Transformation of $HL2^{2-}$ to $HL3^{2-}$ leads to elongation of the original C═N bond from 1.323 to 1.518 Å because of its transformation to the C−N bond. The dangling alcohol functions {(H)O5} and {H(O2)} of $HL3^{2-}$and $HL4^{2-}$ are engaged in hydrogen-bonding interactions with the lattice water O1W and methanol O1A atoms, showing O···O separations of 2.903 and 3.385 Å, respectively (Figure S4 in the SI).

Although the transformation of two metal-bound $HL2^{2-}$ to $HL3^{2-}$ and $HL4^{2-}$ was not expected, the formation of these anions can be fully rationalized. The transformation is nickel(II)-coordination-assisted, where in one case $HL2^{2-}$ undergoes the nucleophilic addition of Me_2pz^- to one of the imine C atoms to form $HL3^{2-}$. In the other case, the same reaction takes place on the same imine C atom followed by hydrolysis of the imine alcohol arm, resulting in $HL4^{2-}$ (Scheme S2 in the SI). Such coordination-assisted C−N coupling may be useful for the synthesis and isolation of new and novel ligand systems.[21] Transformation of the imine function is important in Mannich-type and other related reactions, cascade processes, and multicomponent reactions involving nitrogen heterocycles of biological significance.[22]

The direct-current magnetic susceptibility data for **1** were recorded between 350 and 1.8 K in an applied field of 1000 Oe. The plot of the χT (where χ is the molar magnetic susceptibility defined by M/H, with M being the magnetization and H the external magnetic field) value at 350 K is equal to 3.9 cm^3 K mol^{-1}, slightly lower than the theoretical value predicted for four noninteracting $S = 1$ centers (4 cm^3 K mol^{-1}) with $g = 2$. With a lowering of the temperature, the χT product decreases monotonously, suggesting dominant antiferromagnetic exchange interactions. Below 10 K, the χT product is almost zero, indicating stabilization of a diamagnetic ground state for the $[Ni_4]$ complex ($S_T = 0$). To model the magnetic properties of **1**, the following isotropic Heisenberg Hamiltonian equation (eq 1) has been used, with J_1 and J_2 being the magnetic interactions between the two phenoxido-bridged Ni^{II} pairs and between the two central Ni^{II} ions, Ni2 and Ni2*, respectively. While no low-field analytical expression for the magnetic susceptibility can be derived from eq 1, the model can fortunately be simplified considering the bridging geometries involving two O atoms in **1** and the available literature data for other double-oxygen-bridged dinuclear nickel(II) complexes.[23]

$$\hat{H} = -2J_1(S_{\mathrm{Ni1}}\cdot S_{\mathrm{Ni2}} + S_{\mathrm{Ni1*}}\cdot S_{\mathrm{Ni2*}}) - 2J_2 S_{\mathrm{Ni2}}\cdot S_{\mathrm{Ni2*}} \qquad (1)$$

The exchange interactions are known to be strongly dependent on the Ni−O−Ni angles, varying from positive to negative values when the angle is increasing with a crossing point at ca. 99°.[23] In **1**, the average Ni−O−Ni angles are 99.4° and 102.17° for the central alkoxido and phenoxido bridges, respectively, suggesting a weaker J_2 interaction than J_1. Therefore, a simplified approach was adopted by neglecting the J_2 exchange interaction in eq 1. In this case, the susceptibility, χ, can be analytically derived in the low-field approximation for simply two $S = 1$ spin dimers.[24] This simplified model allows an excellent fit of the experimental χT versus T data for **1** with $g = 2.09(1)$ and $J_1/k_B = -31.0(1)$ K, as shown by the red line in Figure 2. The sign and magnitude of the exchange coupling J_1 through the phenoxido bridges confirm the presence of significant antiferromagnetic interactions between the Ni1 and Ni2 centers, and the obtained value is in good agreement with the known magnetostructural correlations.[23] Numerical simulations[24] of the χT versus T plot taking into account both J_1 and J_2 (Figure S6 in the SI) lead to the conclusion that the J_2 interaction cannot be precisely determined from the susceptibility measurements. Nevertheless, when J_2 adopts values between +5 and −5 K, the experimental data were correctly reproduced with only small modulations of the J_1 values (−32 and −30 K, respectively). Therefore, the simplified model described

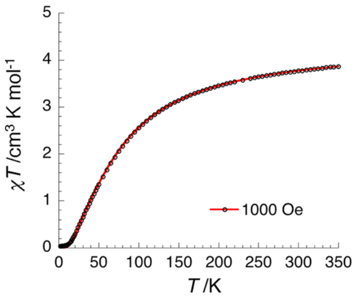


Figure 2. χT versus T plot for complex **1**. The dots are experimental points, and the solid red line represents the best fit of the experimental data.

above gives a reliable estimation of J_1 around the −31 ± 1 K and a 0 ± 5 K window for the J_2 interaction.

Our initial attempts into the use of H_3L2 as a ligand for the synthesis of a dinuclear nickel(II) complex afforded instead a self-assembled zigzag-type tetranuclear nickel(II) complex. The initially used H_3L2 ligand has been transformed into two different species involved in the coordination and self-aggregation of four Ni^{II} ions in a staircaselike geometry. To the best of our knowledge, this $[Ni_4]$ complex is the first polymetallic complex comprising two different forms of a ligand that has undergone metal-ion-coordination-assisted transformation, without the originally employed ligand being present in the reaction product. Two bimetallic fragments are connected by pyrazolyl alkoxide units derived from pyrazolate attack of the imine C atom followed by alcohol arm hydrolysis. The metal-ion specificity for this type of ligand modification reaction would be diagnosed with other 3d metal ions. In the future, isolation of $HL3^{2-}$ and $HL4^{2-}$ in free form will play a definitive role in the generation of the types and forms of polynuclear 3d and 3d−4f complexes.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic data in CIF format, Tables S1 and S2, Scheme S1−S4, Figures S1−S6, synthesis and characterization of ligand H_3L2, and details of physical techniques. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b00411.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

A.K.G. thanks the Council of Scientific and Industrial Research, New Delhi, India, for financial support. T.S.M. acknowledges the University Grant Commission, New Delhi, India, for a research fellowship. R.C. and C.M. thank the University of Bordeaux, the CNRS, the Région Aquitaine, the ANR, and the Institut Universitaire de France for financial support. V.B. thanks the University of Ferrara for financial support.

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(20) Crystal data for compound $\mathbf{1}\cdot 2MeOH\cdot 2H_2O$: $C_{76}H_{110}Ni_4N_{14}O_{16}$ (M_w = 1710.62), monoclinic, space group $P2_1/c$, a = 12.342(3) Å, b = 13.667(3) Å, c = 24.784(5) Å, β = 90.776(6)°, V = 4180.1(15) Å^3, Z = 2, D_c = 1.359 g cm^{-3}, μ = 9.58 cm^{-1}, 33554 reflections collected, 7029 unique (R_{int} = 0.2014), R_1 (obsd reflections) = 0.0870, wR_2 (all reflections) = 0.2929. All non-H atoms were refined anisotropically except some C and O atoms, belonging to alcohol arms and CH_3OH solvent molecules, which were found disordered and refined isotropically over two positions. CCDC 869971.

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(24)

$$\chi_{2Ni_2} = 2\frac{N{\mu_B}^2 g^2}{k_B T}\,\frac{2e^{2J_1/k_BT} + 10e^{6J_1/k_BT}}{1 + 3e^{2J_1/k_BT} + 5e^{6J_1/k_BT}}$$