

RESEARCH ARTICLE



Cite this: *Inorg. Chem. Front.*, 2020, 7, 247

In situ transformation of a tridentate to a tetradentate unsymmetric Schiff base ligand via deaminative coupling in Ni(II) complexes: crystal structures, magnetic properties and catecholase activity study†

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A new dimeric Ni(II) complex, $[\text{Ni}_2\text{L}^1_2(\text{CH}_3\text{CN})_4](\text{ClO}_4)_2 \cdot 2\text{CH}_3\text{CN}$ (**1**), was synthesized using an N_2O donor reduced Schiff base $[(\text{HL}^1) = 2\text{-}[(3\text{-methylamino-propylamino-methyl})\text{-4-phenol}]$. Surprisingly, during an attempt to replace its ClO_4^- ion with SCN^- , the N_2O donor ligand *in situ* converted to a tetradentate N_2O_2 donor ligand and formed a metal complex, $[\text{Ni}(\text{HL}^2)(\text{NCS})(\text{CH}_3\text{CN})]$ (**2**). A probable mechanism *via* deaminative coupling for this conversion is proposed. Using **2** as a metalloligand under basic conditions, a trinuclear metal complex, $[\text{Ni}_3(\text{L}^2)_2(\text{NCS})_2(\text{H}_2\text{O})_4] \cdot \text{H}_2\text{O}$ (**3**), was prepared. Single crystal structural characterization revealed that in all three metal complexes, the Ni(II) atoms were in an octahedral environment with coordinated solvent molecules (CH_3CN in **1** and **2** and H_2O in **3**). Among the three metal complexes, **1** and **3** showed catecholase-like biomimicking activity. The calculation of the turnover numbers ($K_{\text{cat}} = 7.9$ for **1**, 14.5 for **3**) reveals that **3** is a better catalyst than **1**. Mechanistic cycles are proposed for this biomimicking activity on the basis of ESI-MS spectrometry and iodometric measurements. Temperature-dependent magnetic susceptibility measurements suggest that the Ni(II) ions in metal complexes **1** and **3** are antiferromagnetically coupled ($J = -32.22 \text{ cm}^{-1}$ for **1**, $J = -10.4 \text{ cm}^{-1}$ for **3**), consistent with their geometries and bridging angles. Theoretically calculated J values ($J = -40.15 \text{ cm}^{-1}$ for **1**, $J = -14.53 \text{ cm}^{-1}$ for **3**) by the DFT method corroborate well with the experimental values.

Received 2nd August 2019,
Accepted 23rd October 2019

DOI: 10.1039/c9qi00975b

rscl/frontiers-inorganic

Introduction

N,O-Donor ligands have been widely designed and used for the synthesis of the coordination complexes of predetermined nuclearity and stereochemistry depending upon the type of metal ions.¹ However, from a synthetic viewpoint, this synthesis is not free from unexpected outcomes, such as struc-

tural serendipity,² *in situ* ligand transformation,³ and the formation of carbonato-bridged complexes by atmospheric CO_2 fixation.⁴ Structural serendipity is encountered very often during inorganic synthesis; however, the transformation of organic ligand scaffolds has also been observed on few occasions, which opens up new avenues of metal-assisted catalytic transformation to obtain value-added chemicals. These *in situ* ligand transformations mostly depend on the reactivity of the functional groups towards nucleophilic addition,⁵ hydro-/solvolysis,⁵ cycloaddition,^{5,6} isomerisation,⁷ elimination,⁸ oxidation,⁹ reduction,¹⁰ and condensation¹¹ as well as substitution on aromatic side chains.¹² The metal ion often plays a very important role in such transformations.¹³ For example, strongly Lewis acidic redox-inactive metal ions are known to activate the electrophilic center of the imine group of a Schiff base, giving rise to nucleophilic addition.^{14,15} These transition metal ion-catalyzed coupling reactions have important synthetic applications in single step organic transformation.¹⁶

We have been using N_2O -donor Schiff bases for quite some time to synthesize polynuclear transition metal complexes

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† Electronic supplementary information (ESI) available: ESI-MS spectra of metal complexes **1**–**3**; different reaction mixtures as well as spectra of complexes **1** and **3** with 3,5-DTBC; table of the bond parameters of complexes **1**–**3**; different plots and mechanistic cycle of **1** for catecholase activity; magnetization and correlation plots of **1** and **3**; table of kinetic parameters for the catecholase activity of **1** and **3**. CCDC 1944919–1944921. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c9qi00975b