



Mendeleev Communications

## Synthesis, characterization and catalytic activity of a heterometallic Ni/Zn compound in the H/D exchange of salicylaldehyde

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DOI: 10.1016/j.mencom.2014.06.011

The heterometallic Ni/Zn compound  $[Ni(bpy)_3][Zn(NCO)_4] \cdot H_2O$  was synthesized and crystallographically characterized. This complex is an efficient catalyst in the H/D exchange reaction of salicylaldehyde, as confirmed by <sup>1</sup>H NMR spectroscopy and GC-MS analysis.

The self-assemblies of organic and inorganic molecules are of interest in crystal engineering.<sup>1-3</sup> Hydrogen bond interactions play an important role in structural organization by producing a wide range of dimensional networks.<sup>4-6</sup> Many coordination polymers constructed from transition metals and pseudohalide ligands such as azide and thiocyanate have been reported.<sup>7–11</sup> The cyanate complexes are known but less developed among the bridging pseudohalide compounds.<sup>12</sup> The coordination modes of cyanate vary from terminal to bridging and from end-to-end to end-to-on modes.<sup>13</sup> This coordinative flexibility is ideal in selfassembly syntheses. Stabilized by hydrogen bonds, these compounds possess high dimensional structures. The heterometallic compounds are applicable in the production of magnetic<sup>14</sup> and photoluminescence materials,15 electrochemistry and catalysis.16,17 Various coordination compounds were used as catalysts in H/D exchange reactions.18,19

Here, we examined the self- and competitive selectivity of Ni<sup>II</sup> and Zn<sup>II</sup> towards bpy and cyanate with the formation of an ion-pair complex between the metals and the catalytic activity of the complex in the H/D exchange of salicylaldehyde.

Complex 1 was obtained from the reaction of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O, 2,2'-bipyridine and NaOCN in a molar ratio of 1:1:3:2. The crystal structure of compound 1 was determined by a single-crystal X-ray diffraction study (Figure 1).<sup>†</sup> The complex consists of a [Ni(bpy)<sub>3</sub>]<sup>2+</sup> cation, a [Zn(NCO)<sub>4</sub>]<sup>2-</sup> anion and a disordered water hydrate. The nickel(II) center is six-coordinated and slightly distorted from ideal octahedral. The [Zn(NCO)<sub>4</sub>]<sup>2-</sup> anion is tetrahedral. In addition, each water molecule is involved in two hydrogen bonds formed by the hydrogen atoms of water



Figure 1 Molecular structure of 1. Selected bond lengths (Å) and angles (°): Ni(1)–N(1) 2.079(2), Ni(1)–N(2) 2.083(2), Ni(1)–N(3) 2.090(2), Ni(1)–N(4) 2.093(2), Ni(1)–N(5) 2.100(2), Ni(1)–N(6) 2.075(2), Zn(1)–N(7) 1.973(3), Zn(1)–N(8) 1.962(4), Zn(1)–N(9) 1.954(4), Zn(1)–N(10) 1.951(3); N(1)–Ni(1)–N(2) 78.56(9), N(1)–Ni(1)–N(3) 95.44(9), N(1)–Ni(1)–N(4) 171.30(9), N(6)–N(1)–N(3) 169.51(9), N(2)–N(1)–N(5) 172.31(9), N(1)–Ni(1)–N(5) 98.27(9), N(1)–Ni(1)–N(6) 92.90(9), N(7)–Zn(1)–N(8) 107.94(14), N(7)–Zn(1)–N(9) 110.46(16), N(8)–Zn(1)–N(10) 110.57(15), N(6)–C(30)–C(29) 123.3(3), N(7)–C(31)–O(1) 177.1(4), N(8)–C(32)–O(2) 179.4(5), N(9)–C(33)–O(3) 177.4(6), N(10)–C(34)–O(4) 178.9(4).

and the oxygen atoms of cyanate ligands. These H-bonding interactions stabilize the structure by linking the dianions together and extending into a one-dimensional chain along the *c* axis (Figure S1, Online Supplementary Materials). As shown in the crystal packing, the  $[Ni(bpy)_3]^{2+}$  cation units reside in the vacancy between anion chains (Figure S2).

Compound 1 was used as a catalyst in the H/D exchange reaction of salicylaldehyde and DMSO- $d_6$ . The reaction was monitored using <sup>1</sup>H NMR spectroscopy.<sup>‡</sup> Immediately, the hydroxyl proton signal at 10.67 ppm diminishes and shows a broad peak.

 $Zn(OAc)_2 \cdot 2H_2O$  (0.0008 g, 0.0038 mmol, 3 mol%) and Ni(NO<sub>3</sub>)<sub>2</sub>  $\cdot 6H_2O$  (0.0011 g, 0.0038 mmol 3 mol%) were tested as a catalyst in the reaction.

<sup>&</sup>lt;sup>†</sup> For detailed procedure and characteristics of complex **1**, see Online Supplementary Materials.

*Crystallographic data for* **1**: at 223(2) K crystals of  $C_{34}H_{26}N_{10}NiO_5Zn$  are orthorhombic, space group *Pbcn*, *a* = 14.4246(6), *b* = 20.1323(9) and *c* = 23.6131(11) Å, *V* = 6857.3(5) Å<sup>3</sup>, *Z* = 8, *M* = 778.73, *d*<sub>calc</sub> = 1.509 g cm<sup>-3</sup>,  $\mu$ (MoK $\alpha$ ) = 1.306 mm<sup>-1</sup>, *F*(000) = 3184. Diffraction data were collected on a Bruker AXS APEX diffractometer equipped with a CCD detector using graphite-monochromated MoK $\alpha$  radiation [ $\lambda$ (MoK $\alpha$ ) = 0.71073 Å]. The refinement converged to *wR*<sub>2</sub> = 0.1253, GOF = 1.035 for all independent reflections [*R*<sub>1</sub> = 0.0506 was calculated against *F* for 7876 observed reflections with *I* > 2*σ*(*I*)].

CCDC 936775 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2014.

<sup>&</sup>lt;sup>‡</sup> *Catalytic activity*. [Ni(bpy)<sub>3</sub>][Zn(NCO)<sub>4</sub>]·H<sub>2</sub>O 1 (0.0030 g, 0.0038 mmol, 3 mol%) was dissolved in DMSO- $d_6$  (*ca.* 0.4 ml) and transferred into an NMR tube. Salicylaldehyde (13.40 µl, 0.1260 mmol) was injected into the tube. The progress of the reaction was monitored by <sup>1</sup>H NMR spectroscopy. The organic product was identified by NMR spectroscopy and GC-MS analysis. <sup>1</sup>H NMR (DMSO- $d_6$ )  $\delta$ : 10.23 (1H, CH), 7.65 (1H, H<sub>Ar</sub>), 7.49 (1H, H<sub>Ar</sub>), 6.98 (2H, H<sub>Ar</sub>). <sup>13</sup>C NMR (DMSO- $d_6$ )  $\delta$ : 192 (CH), 161 (C), 136 (CH), 129, 124 (C), 122 (CH), 119 (CH), 117 (CH). EI-MS (70 eV), *m*/*z* (%): 123 (23), 121 (100), 65 (15).



**Figure 2** <sup>1</sup>H NMR spectrum of salicylaldehyde- $d_1$ .



Figure 3 The HSQC spectrum and proposed structure of salicylal dehyde- $d_1$ .

After 5.5 h, the hydroxyl proton peak completely disappears and other peaks remain unchanged (Figure 2). From HSQC spectrum, all positions of C and H are the same as those of salicylaldehyde except no proton at hydroxyl group (Figure 3). The peak assignment indicated in the spectrum tentatively suggests the structure of salicylaldehyde- $d_1$ . To confirm the H/D exchange reaction of the salicylaldehyde, the organic product was analyzed by GC-MS (Figure S3). The product ion of m/z 123 at a retention time of 22.20 min produces fragment ions with m/z 121 and 65. They resulted from the loss of a deuterium atom from the ion at m/z 123 and the formation of the  $[M-C_5H_5]^+$  ion, respectively. Since the molecular weight of salicylaldehyde is 122, only one active H in its structure was exchanged for a deuterium atom. The similar reaction was also performed using DMSO. The product ion mass spectrum of m/z 122 at a retention time of 20.92 min shows fragment ions at m/z 121 and 65 (Figure S4). However, the molecular ion of m/z 123 was found in this reaction. The intensity of this ion in DMSO- $d_6$  is higher than that in DMSO. The molecular weight of salicylaldehyde- $d_1$  causes a slow mobility of the substance and results in an increase of the retention time.<sup>20</sup> The GC-MS analysis and <sup>1</sup>H NMR spectroscopy confirmed the H/D exchange reaction. Ni(NO3)2·6H2O or Zn(OAc)2·2H2O was tested as a catalyst under identical conditions (Figure 4). The hydroxyl proton immediately manifests itself as a broad peak at 10.67 ppm in the presence of Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O and this peak remained unchanged after 6 h. When using Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O as a catalyst, there is no reaction after 6 h. Thus, the heterometallic ion pair compound is an efficient catalyst in the H/D exchange of salicylaldehyde. Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O can also catalyze the H/D exchange reaction, however, the reaction is not complete within 6 h. The Lewis acidity of the zinc salt may be the source for promoting the catalytic activity. Other alcohol substrates, namely, tert-butanol, diphenylmethanol and phenylethanol were tested under analogous conditions with complex 1 as a catalyst, but no reaction was observed within 6 h.



Figure 4 The <sup>1</sup>H NMR spectra of the H/D exchange of salicylaldehyde in the presence of 1,  $Zn(OAc)_2 \cdot 2H_2O$  or  $Ni(NO_3)_2 \cdot 6H_2O$ .

Innovation in Chemistry (PERCH-CIC). We are grateful to Miss Tan Geok Kheng and Hong Yimian (National University of Singapore) for the solution of the crystal structure.

## **Online Supplementary Materials**

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2014.06.011.

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This work was supported by Khon Kaen University under Incubation Researcher Project and the Center of Excellence for

Received: 12th August 2013; Com. 13/4177