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

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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 ^1H NMR spectroscopy and GC-MS analysis.

The self-assemblies of organic and inorganic molecules are of interest in crystal engineering.[1–3] Hydrogen bond interactions play an important role in structural organization by producing a wide range of dimensional networks.[4–6] Many coordination polymers constructed from transition metals and pseudohalide ligands such as azide and thiocyanate have been reported.[7–11] The cyanate complexes are known but less developed among the bridging pseudohalide compounds.[12] The coordination modes of cyanate vary from terminal to bridging and from end-to-end to end-to-on modes.[13] This coordinative flexibility is ideal in self-assembly syntheses. Stabilized by hydrogen bonds, these compounds possess high dimensional structures. The heterometallic compounds are applicable in the production of magnetic[14] 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^{II} and Zn^{II} 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 $Ni(NO_3)_2\cdot 6H_2O$, $Zn(OAc)_2\cdot 2H_2O$, 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).† The complex consists of a $[Ni(bpy)_3]^{2+}$ cation, a $[Zn(NCO)_4]^{2-}$ anion and a disordered water hydrate. The nickel(II) center is six-coordinated and slightly distorted from ideal octahedral. The $[Zn(NCO)_4]^{2-}$ anion is tetrahedral. In addition, each water molecule is involved in two hydrogen bonds formed by the hydrogen atoms of water 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).

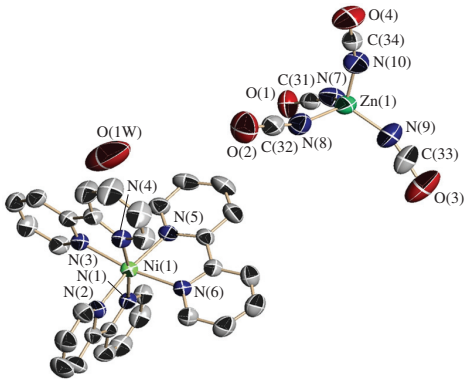

Figure 1 Molecular structure of **1**. Selected bond lengths (Å) and angles (°): Ni(1)–N(1) 2.079(2), Ni(1)–N(2) 2.083(2), Ni(1)–N(3) 2.090(2), Ni(1)–N(4) 2.093(2), Ni(1)–N(5) 2.100(2), Ni(1)–N(6) 2.075(2), Zn(1)–N(7) 1.973(3), Zn(1)–N(8) 1.962(4), Zn(1)–N(9) 1.954(4), Zn(1)–N(10) 1.951(3); N(1)–Ni(1)–N(2) 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) 109.61(15), N(7)–Zn(1)–N(10) 110.91(14), N(8)–Zn(1)–N(9) 110.46(16), N(8)–Zn(1)–N(10) 106.25(15), N(9)–Zn(1)–N(10) 111.57(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).

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

† 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^3, $Z = 8$, $M = 778.73$, $d_{calc} = 1.509$ g cm^{-3}, μ(MoKα) = 1.306 mm^{-1}, $F(000) = 3184$. Diffraction data were collected on a Bruker AXS APEX diffractometer equipped with a CCD detector using graphite-monochromated MoKα radiation [λ(MoKα) = 0.71073 Å]. The refinement converged to $wR_2 = 0.1253$, GOF = 1.035 for all independent reflections [$R_1 = 0.0506$ was calculated against F for 7876 observed reflections with $I > 2\sigma(I)$].

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.

‡ *Catalytic activity.* $[Ni(bpy)_3][Zn(NCO)_4]\cdot H_2O$ **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 ^1H NMR spectroscopy. The organic product was identified by NMR spectroscopy and GC-MS analysis. ^1H NMR (DMSO-d_6) δ: 10.23 (1H, CH), 7.65 (1H, H_{Ar}), 7.49 (1H, H_{Ar}), 6.98 (2H, H_{Ar}). ^{13}C NMR (DMSO-d_6) δ: 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).

$Zn(OAc)_2\cdot 2H_2O$ (0.0008 g, 0.0038 mmol, 3 mol%) and $Ni(NO_3)_2\cdot 6H_2O$ (0.0011 g, 0.0038 mmol 3 mol%) were tested as a catalyst in the reaction.

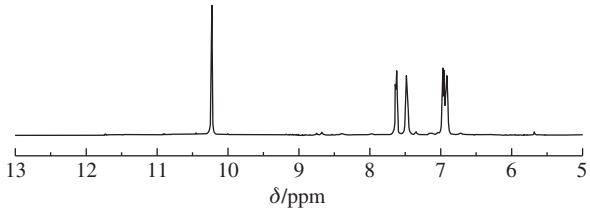

Figure 2 ^{1}H NMR spectrum of salicylaldehyde-d_1.

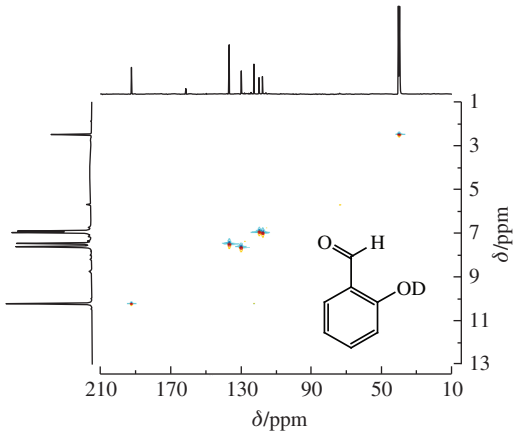

Figure 3 The HSQC spectrum and proposed structure of salicylaldehyde-d_1.

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.[20] The GC-MS analysis and ^{1}H NMR spectroscopy confirmed the H/D exchange reaction. $Ni(NO_3)_2{\cdot}6H_2O$ or $Zn(OAc)_2{\cdot}2H_2O$ 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 $Zn(OAc)_2{\cdot}2H_2O$ and this peak remained unchanged after 6 h. When using $Ni(NO_3)_2{\cdot}6H_2O$ 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. $Zn(OAc)_2{\cdot}2H_2O$ 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.

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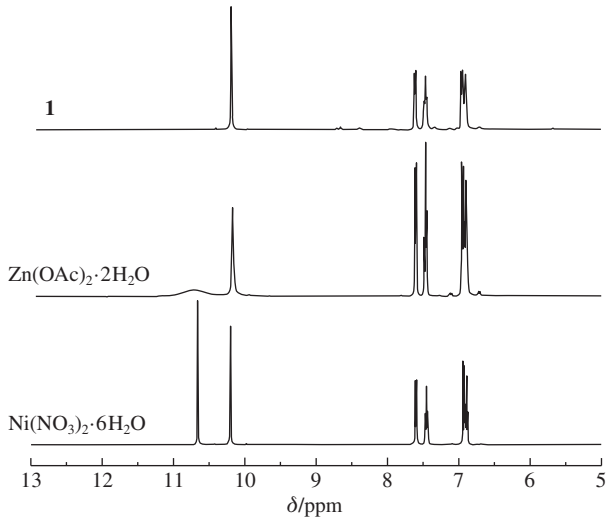

Figure 4 The ^{1}H NMR spectra of the H/D exchange of salicylaldehyde in the presence of **1**, $Zn(OAc)_2{\cdot}2H_2O$ or $Ni(NO_3)_2{\cdot}6H_2O$.

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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