Inorganic Chemistry Communications 33 (2013) 158–160

Contents lists available at SciVerse ScienceDirect

Inorganic Chemistry Communications

journal homepage: www.elsevier.com/locate/inoche

A tetrazolate-based coordination complex with novel 3D structure and catalytic property

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ARTICLE INFO

Article history:
Received 14 January 2013
Accepted 18 March 2013
Available online 12 April 2013

Keywords:
Metal–organic framework
Tetrazole
Crystal structure
Catalysis

ABSTRACT

Hydrothermal reaction of 5-(4-nitrophenyl)-2H-tetrazole [H(4-nptz)] and CuCl generates a novel complex Cu(4-nptz). In complex (**1**), the tetrahedral Cu(I) cations are linked by μ_4-4-nptz ligands into a 4-connected 3D framework with sra topology. Complex (**1**) represents the first 3D structure constructed by 4-nptz ligand, and it is insolvable in all solutions and stable in room temperature. However, it will explode when the temperature is higher than 360 °C. UV–vis diffuse reflectance spectroscopy (DRS) of complex (**1**) exhibits a strong absorption band in the visible light region around 750 nm. In addition, complex (**1**) exhibits catalytic property to the hydrolysis of ester.

The design and assembly of metal–organic frameworks (MOFs) have attracted great interests over recent years, because of their intriguing architectures as well as the potential applications in catalysis, magnetism, luminescence, ion exchange, and gas storage [1–4]. As it is well known, the choice of organic ligands is one of the most crucial factors for the construction of novel topological structures. A comprehensive research of MOFs built on tetrazoles and their derivatives has witnessed tremendous attention since the preparation of the first tetrazole complex by the Bladin in 1885 [5]. The multi nitrogen atoms of tetrazoles and their derivatives endow them rich coordination modes to act as either a multidentate or a bridging building block for constructing high dimensional frameworks with a wide diversity of topologies [6–10].

5-(4-Nitrophenyl)-2H-tetrazole [H(4-nptz)] possesses one tetrazolate ring and one nitro group, which represents a significant multidentate tetrazolate ligand to synthesis MOFs. However, the H(4-nptz) ligand has not been well exploited in building coordination complexes, only one relevant report is available up to date [11]. In our attempt to synthesize high dimensional coordination polymer based on H(4-nptz) and d^{10} metal Cu(I), a novel complex, Cu(4-nptz) (**1**) with 3D sra framework was obtained. In addition, it exhibits catalytic property to the hydrolysis of ester. To our best knowledge, it represents the first 3D structure constructed by 4-nptz ligand.

The hydrothermal reaction of CuCl and H(4-nptz) at 140 °C for 3 days produced red brown needle-like crystals [12,13]. Single-crystal X-ray diffraction analysis reveals that complex (**1**) crystallizes in monoclinic system with $P2_1/c$ space group [14,15]. The asymmetric unit of **1** is composed of one Cu(I) cation and one 4-nptz ligand. The Cu1 ion is four-coordinated in a distorted tetrahedron geometry defined by three N atoms and one O atom from four different 4-nptz ligands with the Cu–N bond lengths of 1.969(2)–2.046(2) Å and Cu–O = 2.477(2) Å (Fig. 1) respectively.

In the crystal packing, initially, the tetrazolate group of the 4-nptz ligand serves as a tridentate bridging linker, which coordinates with three different Cu(I) cations to form a 2D layer {tetrazole-Cu} moiety. It can be seen as a fes-type network, when the tetrazolate group is reduced as a 3-connected node. Furthermore, the nitro group of 4-nptz ligand takes part in the coordination of Cu(I) cation, which links the adjacent 2D layer to form a 3D framework (Fig. 2). The 4-nptz-based metal complexes, $[Cd(H_2O)_2(4\text{-nptz})_2]\cdot 2(H_2O)$ and $[Cd(H_2O)_2(4\text{-nptz})_2]$, were first reported in 2009 [11], in which the nitro group acts as an accepter of hydrogen bonds instead of coordination group to form low dimensional structures. To our best knowledge, the reports about nitro groups of aromatic compounds coordinating with transition metals are relatively rare.

In the 4-nptz molecule, the nitrophenyl group twists out of the tetrazolate plane with a dihedral angle of 34.9(2)°. If 4-nptz molecule is assigned as a 4-connected nodes, the 3D structure of complex (**1**) could be regarded as a uninodal 4-c framework of sra-type topology (also called $SrAl_2$, $CeCu_2$ and ABW) with the Schlafli symbol of (4^2; 6^3; 8) (Fig. 3) [16].

The molar conductivity measurements, XPS, PXRD and TGA are carried out to investigate the purity and stability of complex (**1**). The molar conductivity value recorded 12.9 S cm^2 mol^{-1} in DMSO solution at room temperature confirm that complex (**1**) is non-electrolyte and therefore remained neutral and do not undergo ligand exchange with the solvent during the timeframe of the conductivity measurement [17]. The XPS spectra of complex (**1**) are shown in Figure S2 in

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http://dx.doi.org/10.1016/j.inoche.2013.03.016

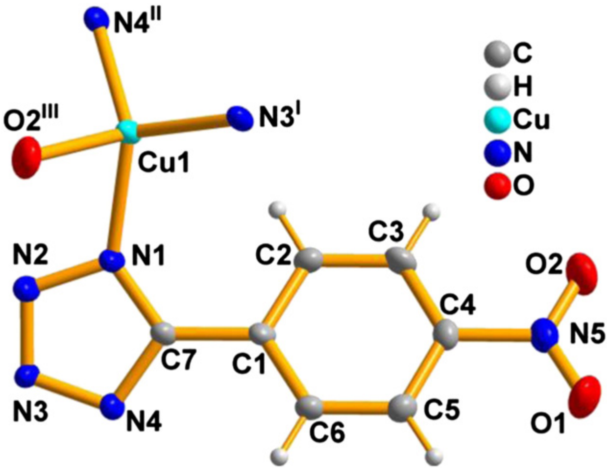
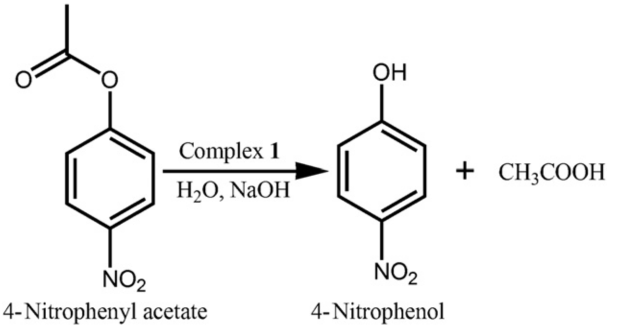


Fig. 1. Asymmetric unit of complex (**1**) with thermal ellipsoids presented at the 50% probability level. Symmetry code: (I) x, 0.5 − y, −0.5 + z; (II) 2 − x, 0.5 + y, 0.5 − z; (III) 1 + x, 0.5 − y, 0.5 + z.

Supporting information. The spin-orbit components ($2p_{3/2}$ and $2p_{1/2}$) of Cu2P peaks were documented at 931.9 and 951.7 eV with a spin-orbit separation of 19.8 eV. It confirms the presence of Cu(I) in complex (**1**) [18,19]. The result of PXRD shows that the peak positions and their intensities are consistent with the simulated pattern, indicating the phase purity of complex (**1**) (Fig. S3). TGA experiments were carried out under N_2 atmosphere to determine the thermal stabilities of complex (**1**). TGA shows complex (**1**) can be stable to 360 °C. The UV–vis diffuse reflectance spectroscopy (DRS) of complex (**1**) was carried out using a Cary 5000 UV–vis-NIR analyzer. As shown in Fig. S4, complex (**1**) exhibits a strong absorption band in the visible light region around 750 nm possibly due to LMCT transition [20], resulting in the red brown color of the complex (**1**).

Though a great number of MOFs have been reported over the past decade, their application as homogeneous or heterogeneous catalysts is relatively rare. Considering practical advantages of easy handling and simple separation from the reaction system, we have examined the synthesized of complex (**1**) act as potential heterogeneous catalyst for the hydrolysis of 4-nitrophenyl acetate (Eq. (1)) [21].



(1)

All products were determined by high performance liquid chromatography (HPLC), compared with authentic samples. Complex (**1**) can enhance the hydrolysis speed of 4-nitrophenyl acetate approximately 3 times when reacting for 30 min compared with blank experiment. After 2 h, the 4-nitrophenyl acetate could completely be converted to 4-nitrophenol with complex (**1**) acting as catalyst. However, in the blank experiment, 38% 4-nitrophenyl acetate is still remained unreacted. This observation encourages us to construct new MOFs that might be efficiently used as heterogeneous catalysts friendly to the environment.

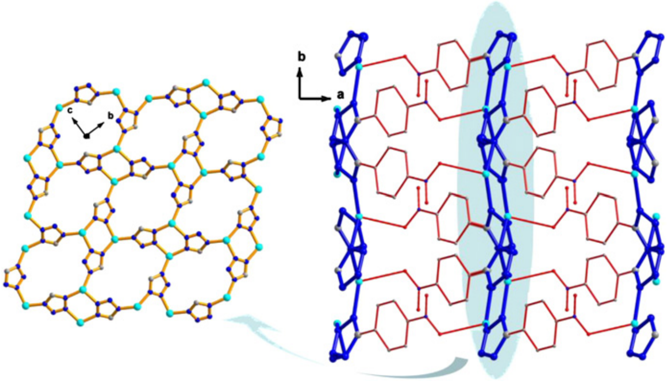


Fig. 2. 3D framework formed by the nitro group coordinating with 2D {tetrazole-Cu} moieties.

In conclusion, a novel complex, Cu(4-nptz) **1** [4-nptz = 5-(4-nitrophenyl)-2H-tetrazole], is synthesized and structurally characterized. In complex (**1**), the 4-nptz ligands act as μ_4-linkages bridging the Cu(I) ions to form a 3D framework with the sra topology. The nitro group of the 4-nptz ligand takes part in the coordination, such coordination model of nitro containing compounds is rarely observed, which plays an important role in the formation of high dimensional structure of complex (**1**). Complex (**1**) is unsolvable in all solutions and stable in room temperature. However, it will explode when the temperature is higher than 360 °C. The catalytic experiment exhibits that complex (**1**) could reduce the reaction time and improve the product yield in the hydrolysis of 4-nitrophenyl acetate.

Acknowledgment

We acknowledge the support of the Natural Science Foundation of Heilongjiang Province (B201108) and Science and Technology Planning Project of Heilongjiang Province (WJ09B03). We thank Heilongjiang University for supporting this study.

Appendix A. Supplementary material

CCDC 918204 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Fig. S1–S4 can be found in the supporting file. Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.inoche.2013.03.016.

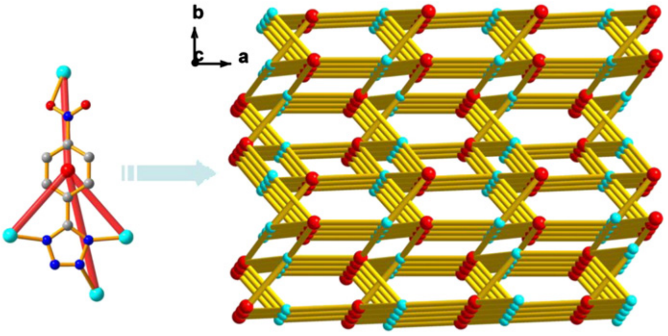


Fig. 3. Schematic illustration of 3D 4-connected sra type topology framework with a Schlafli symbol of (4^2; 6^3; 8).

References

[1] A. Phan, C.J. Doonan, F.J. Uribe-romo, C.B. Knobler, M. O'Keeffe, O.M. Yaghi, Acc. Chem. Res. 43 (2010) 58–67.

[2] J.P. Zhang, Y.B. Zhang, J.B. Lin, X.M. Chen, Chem. Rev. 112 (2012) 1001–1033.

[3] M.P. Suh, H.J. Park, T.K. Prasad, D.W. Lim, Chem. Rev. 112 (2012) 782–835.

[4] B.L. Chen, S.C. Xiang, G.D. Qian, Acc. Chem. Rev. 43 (2010) 1115–1124.

[5] J.A. Bladin, Ber. Dtsch. Chem. Ges. 18 (1885) 1544–1551.

[6] H. Zhao, Z.R. Qu, H.Y. Ye, R.G. Xiong, Chem. Soc. Rev. 37 (2008) 84–100.

[7] T.L. Hu, Y. Tao, Z. Chang, X.H. Bu, Inorg. Chem. 50 (2011) 10994–11003.

[8] X.L. Wang, N. Li, A.X. Tian, J. Ying, D. Zhao, X.J. Liu, Inorg. Chem. Commun. 25 (2012) 60–64.

[9] J.R. Li, Y. Tao, Q. Yu, X.H. Bu, H. Sakamoto, S. Kitagawa, Chem. Eur. J. 14 (2008) 2771–2776.

[10] H. Deng, Y.C. Qiu, Y.H. Li, Z.H. Liu, R.H. Zeng, M. Zeller, S.R. Batten, Chem. Commun. (2008) 2239–2241.

[11] Synthesis of 5-(4-nitrophenyl)-2H-tetrazole ligand [H(4-nptz)]: A mixture of 4-nitrobenzonitrile (7.40 g, 80 mmol), NaN$_3$ (5.20 g, 80 mmol) and NH$_4$Cl (4.28 g, 85 mmol) in DMF (120 mL) was stirred at 120–130 °C for 24 h. After cooling to the room temperature, the reactant was filtered. After that, the filtrate was evaporated, and then the residual solution was pouring into water (10 mL) with constant stirring to give raw product. The raw product was dissolved in ethanol (500 mL) and the residue was filtered out. The ethanol was removed by rotary evaporation to give pale yellow solid substance. Yield: 9.17 g (60% based on 4-nitrobenzonitrile). Element Analysis: Calc. for C$_7$H$_5$N$_5$O$_2$: C, 43.98; H, 2.64; N, 36.64%. Found: C, 43.87; H, 2.72; N, 36.58%. IR (KBr, cm^{-1}): 3205 (m), 3105 (m), 2909 (w), 1607 (m), 1550 (m), 1513 (s), 1339 (s), 1291 (m), 1110 (w), 1062 (w), 993 (w), 859 (m), 730 (w), 700 (w), 531 (w), 498 (w). ^{1}H-NMR (400 MHz, DMSO): 8.43 (2H, s), 8.29 (2H, s), N-bond H atom was not observed.

[12] Synthesis of complex (**1**): H(4-nptz) (95 mg, 0.5 mmol) and CuCl (100 mg, 1.0 mmol), were dissolved in water (10 mL) and the pH value of the mixture solution was carefully adjusted to about 4.5 with 4 mol/LHCl. Then the reaction mixture was heated at 140 °C for three days in a sealed 18 mL Teflon-lined stainless steel vessel under autogeneous pressure. After slow cooling to room temperature, red brown needle-like crystals were filtered and washed with distilled water and ethanol (46% yield based on Cu). Elemental Analysis: Calc. for C$_7$H$_4$CuN$_5$O$_2$: C, 33.14%; H, 1.59%; N, 27.61%. Found: C, 33.02%; H, 1.65%; N, 27.55%. IR (KBr cm^{-1}): 3079 (w), 1601 (m), 1511 (s), 1442 (w), 1333 (s), 1282 (w), 1099 (w), 1008 (w), 870 (m), 733 (m), 691(w), 497 (w). Molar conductivity: 12.9 S cm^2 mol^{-1} in DMSO solution at room temperature.

[13] The X-ray diffraction measurements for complex (**1**) was carried out on a Rigaku R-AXIS RAPID imaging plate diffractometer with graphite-monochromated Mo Kα ($\lambda = 0.71073$ Å) at 291 K. Empirical absorption corrections based on equivalent reflections were applied. The structure of complex (**1**) was solved by direct methods using SHELXS 97. All nonhydrogen atoms were refined anisotropically by the full-matrix least-squares method on F^2. H atoms bound to C atoms were placed in calculated positions and treated as riding on their parent with C−H = 0.93 Å (aromatic), and with U_{iso} (H) = 1.2 U_{eq} (C). Complex (**1**): monoclinic, space group $P2_1/c$, a = 7.7763(3) Å, b = 11.1174(3) Å, c = 9.2900(2) Å, $\beta = 93.539(3)°$, V = 805.94(4) Å^3, Z = 4, Dc = 2.091 g/cm^{-3}, 3386 reflections measured, 1718 independent reflections (Rint = 0.0266), R1 [$I > 2\sigma(I)$] = 0.0340, wR2 = 0.0638, COF = 1.040.

[14] G.M. Sheldrick, Acta Crystallogr. A64 (2008) 112–122.

[15] J. Xiao, W.X. Wang, J.R. Lin, H. Zhao, J. Mol. Struct. 933 (2009) 98–103.

[16] S. Han, J.V. Smith, Acta Crystallogr. A55 (1999) 342–359.

[17] W.J. Geary, Coord. Chem. Rev. 7 (1971) 81.

[18] G.F. Hou, L.H. Bi, B. Li, B. Wang, L.X. Wu, CrystEngComm 13 (2011) 3526–3535.

[19] G.F. Hou, L.H. Bi, B. Li, L.X. Wu, Inorg. Chem. 49 (2010) 6474–6483.

[20] K. Banerjee, K. Biradha, Cryst. Growth Des. 12 (2012) 4264–4274.

[21] Hydrolysis of 4-nitrophenyl acetate was carried out in a one neck round-bottom flask equipped with condenser tube and stirrer. The 4-nitrophenyl acetate (1 mmol) and NaOH (1 mmol) were dissolved in 10 mL distilled water with 0.03 mmol complex (**1**) as catalyst (without catalyst in blank experiment). The mixture was refluxed with stirring, and the products were monitored by HPLC at different time intervals.