Academic Voices
A Multidisciplinary Journal
Volume 7, No. 1, 2017
ISSN 2091-1106

SYNTHESIS AND CHARACTERIZATION OF TWO NEW COORDINATION POLYMERS CONSTRUCTED FROM AZOBENZENE-4, 4′-DICARBOXYLIC ACID WITH ZINC (II) AND CD (II) 2, 2′-BIPYRIDINE

Pramod Kumar Yadav
Department of Chemistry, TU, Thakur Ram Multiple Campus, Birgunj, Nepal
E-mail: pramod_yadav1155@yahoo.com

Abstract

Two transition metal coordination polymers [Zn(4,4′-ADA)(bpy)]n (1) and [Cd(4,4′-ADA)(bpy)(H2O)2]n (2) have been assembled from azobenzene-4,4′-dicarboxylic acid (H2ADA) with the help of 2,2′-bipyridine (bpy) ligand. The different molecular structures for complexes 1 and 2 formed from the same ligand (H2ADA) reveals the fact that organic linkers display different coordination preferences at different metal ions.

Key words

MOFs; azobenzene-4; 4′-dicarboxylic acid; 2, 2′-bipyridine; N,N′-dimethylformamide

Introduction

Metal-organic frameworks (MOFs) or coordination polymers are ordered porous solids in which inorganic building units are joined by organic links (Yaghi *et al.,* 2003). MOFs have received increasing attention because of their intriguing topologies and diverse functionality (Ferey and Serre, 2009). Polycarboxylate aromatic ligands have been successfully employed in the generation of many interesting systems as carboxylic groups can be partially or completely deprotonated, and can coordinate with metal ions in multicoordinated ways (Tranchemontagne *et al.,* 2009). Carboxylates are attractive metal binding units in coordination networks due to the negative charge that significantly enhances their ability to bind strongly to metal centers. MOFs constructed on the skeleton of azo group containing ligands have been found to constitute excellent materials for selective uptake of CO_2 (Nagaraja *et al.,* 2012).

The auxiliary ligands like 2, 2′-bipyridine also impact on the conformations of the flexible carboxylic ligand (Trans- or cis-), and play an important role in the formation of the final structure of the complex. The terminal ligand

2, 2′-bpy tends to construct low-dimension structures which can be extended into high-dimensional supramolecular networks through hydrogen bonds and pi–pi stacking interactions (Kumar *et al.,* 2006).

The metal (Zn, Cd) ions with d^{10} configuration are particularly promising due to their wider range of coordination numbers together with their applications in luminescence and biological activities (Wei *et al.,* 2006; Parkin, 2004). Thus, the present article is thought to be of worth as it deals with the synthesis and characterization of the structures obtained on the skeleton of d^{10} divalent metal (Zn^{II}, Cd^{II}) 2,2′-bipyridines together with azobenzene-4, 4′-dicarboxylic acid.

Experimental section

All reagents and solvents were commercially available and used as received. The carbon, nitrogen, and hydrogen contents of the solid complexes were determined by Carbo-Erba elemental analyzer 1108. The infrared spectra of the complexes were recorded on a Varian 3100 FT-IR spectrometer (4000–400cm–1) using KBr disks. Azobenzene 4,4′-dicarboxylic acid was synthesized following the method used by Ghosh *et al.* (2008) while M(bpy)$(NO_3)_2 \cdot H_2O$ [M =Zn(II)/Cd(II)] was prepared using the procedure as reported by Sen *et al.* (Mitra *et al.,* 1997) for analogous complexes.

The complexes were synthesized by solvothermal reaction (Guo *et al.,* 2006). In a typical synthetic procedure, Zn(bpy)$(NO_3)_2 \cdot H_2O$ (0.381 g, 1.0 mmol) and Cd(bpy)$(NO_3)_2 \cdot H_2O$ (0.428 g, 1.0 mmol) were added to the solution of azobenzene-4,4′-dicarboxylic acid (0.135 g, 0.5 mmol) in N,N'-dimethylformamide (5.0 mL). When the corresponding mixtures were heated at 130–140 °C for 5–7 h, the complexes were isolated in 65–75% yield. They were found insoluble in common organic solvents and were melting above 200 °C.

Scheme 1. Synthetic strategy for complexes.

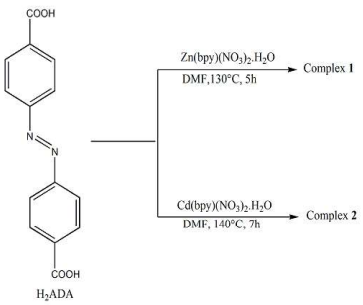

Table 1. Mol. formula, M.P., %yield, elemental analyses and IR data of 1 & 2

Molecular formula of complexes	M.P.(°C)	% Yield	Elemental analyses (%) Calculated (Found) C	H	N	Major IR peaks (ν cm-1)
C24H16N4O4Zn (1)	>200	65	58.89 (58.70)	3.27 (3.10)	11.45 (10.95)	3420(w), 3058(m), 1680(s), 1602(s), 1550(s), 1425(s), 1390(vs),1222(m), 1102(m), 1008(m),856(s),796(s), 720(s), 642(m), 421(m)
C24H20N4O6Cd (2)	>200	75	50.34 (50.28)	3.49 (3.10)	9.79 (10.11)	3398(w), 3060(m), 1600(s), 1548(s), 1429(s), 1389(vs), 1220(m), 1095(m), 865(s), 795(s), 725(s), 640(m), 477(m)

Results and discussion

In infrared spectra of the complexes, the characteristic band of carboxylic acid group observed at 1683 cm^{-1} in the spectrum of free ligand 4,4′-H_2ADA, was absent in the spectra of its complexes. It supported that deprotonated ligands had coordinated with metal ions in the complexes **1**and **2**(Bellamy, 1958). The peaks observed at 1680 and 1600 cm^{-1} in the spectra of complexes **1** and **2** were assigned to ν_{asym} ($-COO^-$) vibration, whereas ν_{sym}($-COO^-$) vibration was observed at 1602 and 1389 cm^{-1}, respectively. Thus, peak separations between ν_{asym}($-COO^-$) and ν_{sym} ($-COO^-$) were found as 75 and 211 cm^{-1}, which supported bis-bidentate and monodentate coordination modes of carboxylate groups, respectively. The spectra of the same complexes showed a peak at 1420 cm^{-1} assigned to the ν(N=N) vibration (Chen *et al.* 2008). The bands observed at 500–480 and 420–380 cm^{-1} were assigned to ν(M–N) and ν(M–O) vibrations, respectively(Nakamoto, 1997).The above experimental results suggest the following structures for the two complexes:

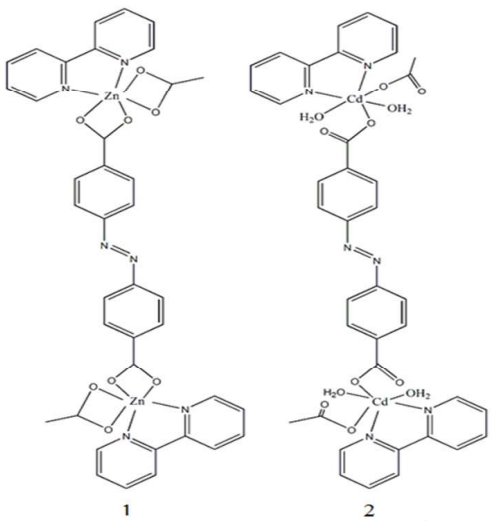

Fig.1: Possible structures for complexes **1***&* **2**

Conclusion

The reaction of metal nitrate containing 2, 2'-bipyridine [metal = Zn^{II}, Cd^{II}] separately with azobenzene-4, 4′-dicarboxylic acid yields two new coordination polymers. These complexes have been characterized by elemental analyses and IR spectroscopy. Since such types of metal–organic frameworks show the formation of porous structures (Kitagawa, 2004), they could be promising candidates as adsorbents for gas separation.

Acknowledgements

The author is thankful to the Head, Department of Chemistry, BHU, Varanasi, India for providing characterization facilities. Thanks are also due to Dr. Ramnath Prasad Yadav, Professor of Chemistry, Tribhuvan University, Nepal for his valuable suggestions and encouragement.

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