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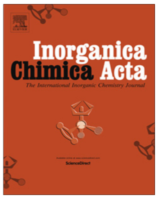

Anion influence in the structural diversity of cadmium coordination polymers constructed from a pyridine based Schiff base ligand

Ali Akbar Khandar [a,*], Farhad Akbari Afkhami [a], Seyed Abolfazl Hosseini-Yazdi [a], Jonathan M. White [b], Scott Kassel [c], William G. Dougherty [c], Janusz Lipkowski [d], Donald Van Derveer [e], Gerald Giester [f], Ferdinando Costantino [g]

[a] Department of Inorganic Chemistry, Faculty of Chemistry, University of Tabriz, Tabriz 51666-16471, Iran
[b] BIO-21 Molecular Science and Biotechnology, University of Melbourne, Parkville, Victoria 3052, Australia
[c] Department of Chemistry, Villanova University, 215 Mendel Science Center, Villanova, PA 19085, USA
[d] Cardinal Stefan Wyszynski University in Warsaw, Faculty of Mathematics and Natural Sciences, Wóycickiego 1/3, 001-938 Warszawa, Poland
[e] Chemistry Department, Clemson University, Clemson, SC 29634-0973, USA
[f] Institute of Mineralogy and Crystallography, University of Vienna, Althanstrasse 14, A-1090 Wien, Austria
[g] Dipartimento di Chimica, Universitá di Perugia, Via Elce di Sotto n. 8, 06124 Perugia, Italy

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ABSTRACT

A series of seven coordination polymers based on Cd and potentially tetradentate pyridine based Schiff base ligand with different anions (CH_3COO^-, NO_2^-, Cl^-, I^-, N_3^-, SCN^-), $[Cd(L)(CH_3COO)(OH_2)]_n$ (**1**),$\{[Cd_2(L)_2(NO_2)_2(CH_3OH)_2]\cdot CH_3OH\}_n$ (**2**), $\{[Cd_2(L)_2Cl_2(CH_3OH)_2]\cdot CH_3OH\}_n$ (**3**), $[Cd(HL)I_2]_n$ (**4**), $[Cd_3(L)_2(N_3)_4]_n$ (**5**), $[Cd(L)(SCN)(OH_2)]_n$ (**6**) and $[Cd(HL)(SCN)_2]_n$ (**7**) {HL = 2-pyridinecarbaldehyde isonicotinoyl hydrazone (HPCIH)} in order to rationalize the effect of the anion, have been synthesized and characterized by elemental analyses, FT-IR spectroscopy, single crystal X-ray data diffraction, etc. The results show the influence of the counter-ions on the coordination mode of the cadmium ion that is capable of forming compounds with five-, six- and seven-coordination numbers. The ligand acts as a negatively charged tetradentate N_3O-donor ligand and coordinates to the cadmium center in the enolic form (=N—N=C—O) in **1**–**3** and **5**–**6** while in compounds **4** and **7** coordinates as N_3- and N_3O-donor neutral ligand in keto form (=N—NH—C=O), respectively. Cadmium centers in **1**–**4** and **6**, bridging by the HPCIH ligand cause to form one-dimensional coordination polymers and the anions act as terminal ligands. In compounds **5** and **7**, the N_3^- and SCN^- also act as bridging ligands to the metal centers, and form 3D and 2D metal–organic polymers respectively.

1. Introduction

In recent years, crystal engineering and construction of coordination polymers (CPs) with fascinating structural topologies have attracted great attention owing to their potential use as functional materials [1]. Crystal engineering has a lot of potential, but it is not possible to predict the outcome of crystallization [2,3]. A major challenge in crystal engineering using polydentate chelating, bridging building blocks is the unpredictability of the polymeric network topology [4] which may depend on several factors such as the coordination geometry and the oxidation state of the metal centers, the metal-to-ligand ratio, the nature of the ligands used, and the presence of solvents and counterions [5–9]. There is still a very long way to go to develop new architectures of coordination polymers using specific spacer ligands in order to rationalize the design of compounds with well-defined structures and useful functions. The ability to predict and control the supramolecular assembly of molecules remains an elusive goal, and much more work is required to understand the inter- and intramolecular forces that determine the patterns of molecular structure and crystal packing. Among the effective factors to design CPs counterions have been paid particular attention in the past few years, since they not only show a co-ligand effect, but also can direct and- or template the formation of assemblies, thus leading to structural diversity [10,11]. Furthermore, some counterions such as carboxylate, nitrate, azide and thiocyanate have various coordination modes and can act as a monodentate, chelate, or bridging ligands within the framework, which may further enrich the structural diversity [10]. Moreover the geometries of organic ligands can have a great

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* Corresponding author. Tel.: +98 411 3346494; fax: +98 411 3340191.
E-mail address: akhandar@yahoo.com (A.A. Khandar).

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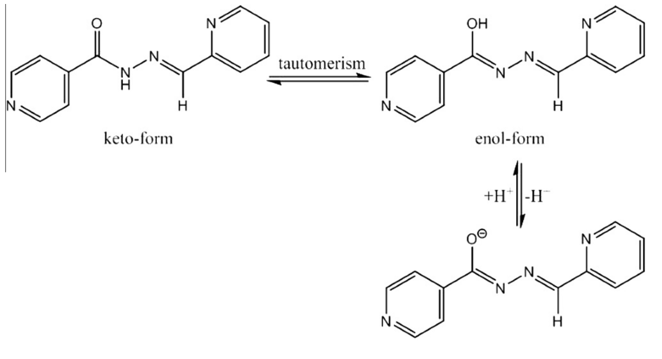


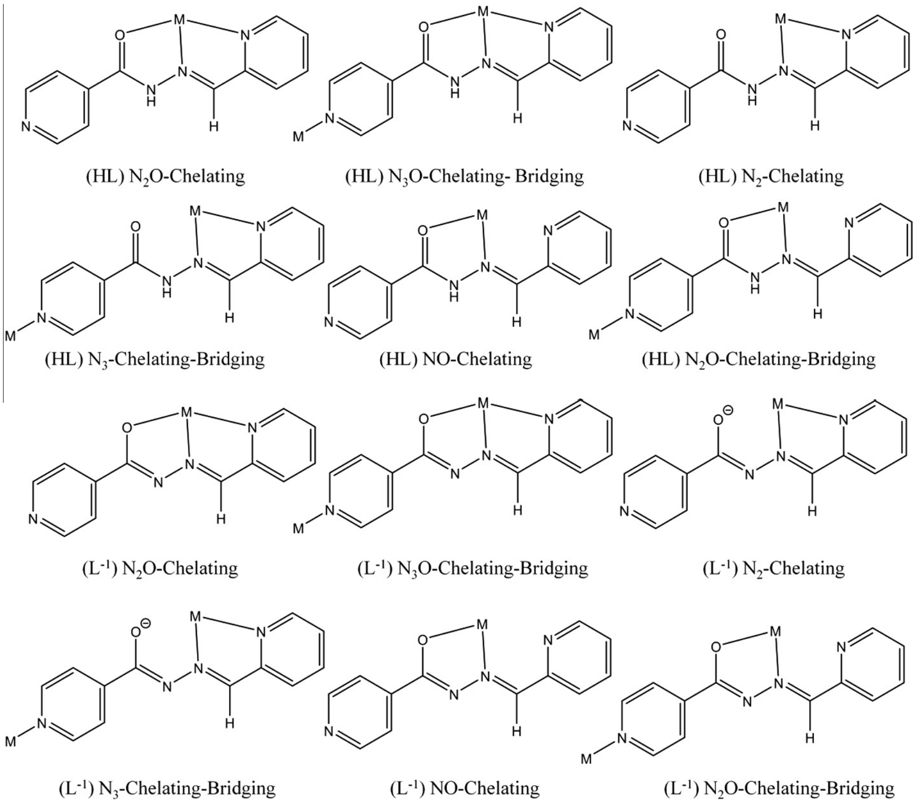
Scheme 1. Structure, keto-enol tautomerism and reversible deprotonation of 2-pyridinecarbaldehyde isonicotinoyl hydrazone (HPCIH).

impact on the structural architecture of coordination polymers [12]; therefore much effort has been devoted to the design and modification of the organic ligands to control the products. Among the organic building blocks bridging blockers, pyridine deriveatives are often used to construct metal-containing supramolecules due to their photophysical and redox properties [4,12,13]. Pyridine based ligands containing amide groups generally are coordinated to the metal centers through their pyridyl nitrogen atoms and interact with each other by hydrogen bonds involving the amide groups, which are important for molecular recognition and constructing supramolecular arrays. On the other hand, as for the d^{10} metal elements, especially for Cd and Zn, they prefer the 2 + oxidation state in most of their complexes, and commonly possess the coordination number from 4 to 8 and the corresponding geometries, which can be utilized to prepare multiform metallosupramolecular complexes [14]. Herein, we describe self-assembly of the potentially tetradentate chelating-bridging ligand (2-pyridinecarbaldehyde isonicotinoyl hydrazone) with divalent cadmium(II) salts as the nodes. The ligand which we have prepared to design and construction of CPs has potential to form different types of complexes due to the multiple coordination sites and the tautomeric effect of enol and keto form (Schemes 1 and 2) [15]. Seven coordination polymers, $[Cd(L)(CH_3COO)(OH_2)]_n$ (**1**), $\{[Cd_2(L)_2(NO_2)_2(CH_3OH)_2]\cdot 2CH_3OH\}_n$ (**2**), $\{[Cd_2(L)_2Cl_2(CH_3OH)_2]\cdot CH_3OH\}_n$ (**3**), $[Cd(HL)I_2]_n$ (**4**), $[Cd_3(L)_2(N_3)_4]_n$ (**5**), $[Cd(L)(SCN)(OH_2)]_n$ (**6**) and $[Cd(HL)(SCN)_2]_n$ (**7**) are prepared. Additionally we show that diversity of anions may cause major changes of the structure and their comparison may be of interest in the design and construction of coordination polymers and may lead to new structures. The role of hydrogen bonding and π…π interaction effects on assembly of metal–organic networks have been also analyzed.

2. Experimental

2.1. Materials and measurements

All the reagents required for syntheses were commercially available and employed without further purification. The hydrazone ligand HPCIH was prepared according to the literature method [16]. Recrystallization from aqueous EtOH afforded pure ligand in >80% yield. Spectroscopic data for HPCIH have been reported [15a]. Elemental analyses were carried out using an Elementar Vario EL III instrument. FT-IR spectra were recorded on a Bruker Tensor 27 FT-IR spectrometer with KBr disks in the range 4000–400 cm^{-1}. The thermal behavior measured with a Netzsch STA449C under static nitrogen atmosphere using platinum pan at a heating rate of 7 °C/min in the noted temperature ranges in Section 3.3.



Scheme 2. Possible coordination modes for 2-pyridinecarbaldehyde isonicotinoyl hydrazone (HPCIH).