Available online at www.sciencedirect.com
SCIENCE DIRECT®
ELSEVIER
Inorganica Chimica Acta 358 (2005) 535–544
Inorganica Chimica Acta
www.elsevier.com/locate/ica

Synthesis, structure and bonding of cadmium(II) thiocyanate systems featuring nitrogen based ligands of different denticity

Suparna Banerjee [a], Biao Wu [b], Paul-G. Lassahn [b], Christoph Janiak [b,*], Ashutosh Ghosh [a,*]

[a] *Department of Chemistry, University College of Science and Technology, University of Calcutta, 92, A.P.C. Road, Kolkata 700 009, India*
[b] *Institut für Anorganische und Analytische Chemie, Universität Freiburg, Albertstr. 21, 79104 Freiburg, Germany*

Received 26 April 2004; accepted 30 July 2004
Available online 21 November 2004

Abstract

Complexes catena-[di(4-amino-pyridine)di(μ-S,N-thiocyanato)cadmium(II)], $^{1}_{\infty}[\mathrm{Cd}(\mu\text{-SCN})_2(\mathrm{L}^1)_2]$ (**1**), catena-[{(1-pyridine-2-yl-ethylene)-hydrazine}di(μ-S,N-thiocyanato)cadmium(II)], $^{1}_{\infty}[\mathrm{Cd}(\mu\text{-SCN})_2(\mathrm{L}^2)]$ (**2**), and di-μ-S,N-thiocyanatobis{(*N,N*-diethyl-*N*′-(1-pyridine-2-yl-ethylidene)-ethane-1,2-diamine)(*N*-thiocyanato)cadmium(II)}, $[\mathrm{Cd(NCS)}(\mu\text{-SCN})(\mathrm{L}^3)]_2$ (**3**) have been synthesized by reacting cadmium acetate/NH_4SCN with 4-amino-pyridine (L^1), $C_5H_4N–C(CH_3){=}NNH_2$ (L^2), and $C_5H_4N–C(CH_3){=}N–CH_2–CH_2–N(C_2H_5)_2$ (L^3), respectively, in methanol. Characterization by single-crystal X-ray crystallography shows that in compounds **1** and **2** the cadmium atoms have a 4N2S-hexa-coordination sphere, exhibiting pseudo-octahedral geometry. The cadmium atoms are bridged by two thiocyanate ions generating 1-D polymeric chains. Compound **3** is a centrosymmetric dimeric complex, with the cadmium atom pseudo octahedrally surrounded by a 5N1S coordination sphere. In compound **1** the crystal packing is controlled mainly by interchain N–H⋯N and C–H⋯π interactions between the aminopyridine moieties, whereas in complexes **2** and **3** π-stacking interactions between the pyridyl planes stabilize the interchain or intermolecular packing, respectively. Thiocyanate and pyridylimine chelation to metal center is also scrutinized with EHMO analysis.

Keywords: Cadmium(II); Thiocyanate; Schiff bases; Bonding; Coordination polymers

1. Introduction

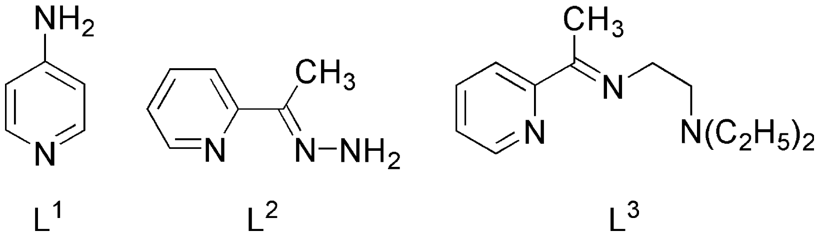
Metal–organic frameworks are widely regarded as promising materials for application in catalysis, separation and molecular recognition [1–4]. In construction of one/two/three dimensional frameworks, multidentate ligands are usually used to bridge metal centers to form polymeric structures. For instance, metal–organic coordination frameworks based on polycarboxylic acid, 4-4′bipyridine and thiocyanates have extensively been studied [5,6]. Coordination polymers of cadmium, with pyridine-type ligands, are also investigated for their fluorescence properties [1,2,7]. Supramolecular contacts such as hydrogen bonding are frequently used as a powerful crystal engineering tool to "control" the packing of the molecular or extended building blocks [8–12]. In addition, π-interactions also offer the propensity for packing control in the solid crystalline state. Aromatic moieties which often occur as part of the organic ligands may either associate via displaced face-to-face π-π [13–17] or edge to face C–H⋯π interactions [18–20].

Cadmium thiocyanate adducts of organic ligands are an important class of compounds for the design and preparation of such functional coordination frameworks,

---

* Corresponding authors. Tel.: +9103323599298; fax: +910333519755.
E-mail addresses: janiak@uni-freiburg.de (C. Janiak), ghosh_59@yahoo.com (A. Ghosh).

0020-1693/$ - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.ica.2004.07.048



Scheme 1.

where Cd(II) forms stable double SCN bridged chains which are usually oriented along one direction [21]. In most cases, monodentate organic ligands, e.g., methyl-substituted pyridines, benzylamine, dibenzylamine, triphenylamine, 1H-1,2,4-triazole, imidazole, etc., were chosen and they occupy the remaining two trans coordination sites [22]. The steric and electronic effects of the monodentate ligands are found to be capable of modifying the chain structure [22]. With monodentate ligands capable of forming additional H-bonds, the chain structure has been extended to higher dimensional hydrogen bonded architectures [23]. On the other hand, propagation of the cadmium thiocyanate chain in the presence of bidentate or tridentate chelating ligands is not well documented [21g].

We report here the synthesis and crystal structure of three Cd(II) thiocyanate complexes with a monodentate ligand, 4-aminopyridine (L^1), a bidentate ligand, $C_5H_4N–C(CH_3)=NNH_2$ (L^2), and a tridentate ligand, $C_5H_4N–C(CH_3)=NCH_2CH_2–N(C_2H_5)_2$ (L^3) (Scheme 1). The ligands were chosen in such a way that they could undergo π–π alignment along with inter-chain H-bonding. The complex with L^3 represents a very rare example of a dimeric species in which Cd atoms are doubly bridged by two NCS ligands.

2. Experimental

2.1. Materials and physical measurements

Commercially available solvents such as 4-aminopyridine, hydrazine monohydrate, 2-acetyl-pyridine, *N,N*-diethylethylenediamine, cadmium acetate dihydrate and ammonium thiocyanate were used without further purification. Elemental analyses were carried out using a Perkin–Elmer 240C elemental analyzer. IR spectra were recorded in KBr (4500–500 cm^{-1}) using a Perkin–Elmer R XI FT-IR spectrophotometer.

2.2. Preparation of ligands

2.2.1. Synthesis of (1-pyridine-2-yl-ethylidene)-hydrazine (ligand L^2)

Hydrazine hydrate (85% aqueous, 0.75 g, 15 mmol) and 2-acetyl-pyridine (1.815 g, 15 mmol) were mixed in methanol (20 ml) and then refluxed for 3 h. The resulting solution was evaporated to 5 ml and cooled to room temperature. Upon cooling the solution, a yellow solid precipitated, was collected by filtration and dried in vacuum over fused $CaCl_2$. Yield: 1.822 g (90%). (Found: C, 62.20; H, 6.62; N, 31.08%. Calc. for $C_7H_9N_3$: C, 62.22; H, 6.66; N, 31.11.) IR (ν/cm^{-1}): 3345–3285 (ν_{NH_2}), 1640 ($\nu_{C=N}$), 1590 (δ_{N-H}), 1447–1302 ($\upsilon_{Pyridine\ ring}$).

2.2.2. Synthesis of N,N-diethyl-N′-(1-pyridin-2-yl-ethylidene)-ethane-1,2-diamine (ligand L^3)

This ligand was prepared by a procedure similar to that for L^2, by starting with *N,N*-diethylethylenediamine (1.74 g, 15 mmol) and 2-acetyl-pyridine (1.815 g, 15 mmol) to obtain a yellow liquid. Light yellow microcrystals were obtained by recrystallization from *n*-hexane. Yield: 2.792 g (85%). (Found: C, 71.20; H, 9.55; N, 19.22%. Calc. for $C_{13}H_{21}N_3$: C, 71.23; H, 9.58; N, 19.17.) IR (ν/cm^{-1}): 1648 ($\nu_{C=N}$).

2.3. Synthesis of metal complexes

2.3.1. $Cd(\mu\text{-}SCN)_2(4\text{-}H_2N–C_5H_4N_2]_\infty$ (**1**)

To a methanol solution (5 ml) of $Cd(OAc)_2 \cdot 2H_2O$ (0.53 g, 2 mmol) was added a methanol solution (10 ml) of NH_4SCN (0.30 g, 4 mmol). The solution was stirred for 10 min and the resultant colorless solution was then added to 15 ml of 4-amino-pyridine (L^1) solution (0.188 g, 2 mmol). The filtrate was allowed to stand in air at room temperature for 24 h, yielding colorless crystals. Yield: 0.388 g (95%). (Found: C, 34.54; H, 2.87; N, 20.15%. Calc. for $C_6H_6Cd_{0.50}N_3S$: C, 34.58; H, 2.88; N, 20.17.) IR (ν/cm^{-1}): 3297–3390 (ν_{NH_2}), 2076 (ν_{SCN}).

2.3.2. $Cd(\mu\text{-}SCN)_2\{2\text{-}C_5H_4N–C(CH_3)=NNH_2\}]_\infty$ (**2**)

$Cd(OAc)_2 \cdot 2H_2O$ (1.33 g, 5 mmol) dissolved in methanol (20 ml) was added to a methanolic solution (10 ml) of NH_4SCN (0.76 g, 10 mmol) followed by ligand L^2 (0.34 g, 2.5 mmol) dissolved in (10 ml) methanol. The mixture was stirred for few minutes and dried in vacuo. Colorless crystals suitable for X-ray diffraction were obtained by dissolving the precipitate in hot DMSO and avoiding light for 24 h. Yield: 1.545 g (85%). (Found: C, 29.70; H, 2.45; N, 19.26%. Calc. for $C_9H_9CdN_5S_2$: C, 29.71; H, 2.47; N, 19.26.) IR(ν/cm^{-1}): 3290–3340 (ν_{NH_2}), 2096 (ν_{SCN}), 1596 ($\nu_{C=N}$).