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Syntheses, structures and magnetic properties of two one-dimensional coordination polymers of cobalt(II) and nickel(II) dicyanamide containing a tridentate N-donor Schiff base

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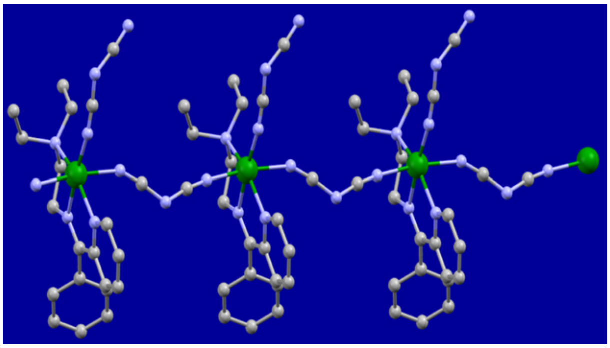
HIGHLIGHTS

- Neutral coordination polymers of cobalt(II) and nickel(II) are isolated using a tridentate Schiff base and dicyanamide.
- X-ray structural studies show that compounds consist of 1D covalent chains formed through single $\mu_{1,5}$-dicyanamide bridges.
- Thermogravimetric analyses reveal their thermal stability and decomposition pattern.
- The compounds show weak antiferromagnetic interactions mediated through dicyanamide bridge.

GRAPHICAL ABSTRACT

Two neutral 1D coordination polymers of the types $[\mathrm{M(L)}(\mu_{1,5}\text{-dca})(\mathrm{dca})]_n$ [M = Co (**1**), Ni (**2**); L = (N,N-diethyl,N′-(pyridin-2-yl)benzylidene)ethane-1,2-diamine; dca = dicyanamide] have been synthesized through one-pot reactions of the building components, and characterized structurally and magneto-structurally.



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ABSTRACT

Two neutral one-dimensional coordination polymers of the type $[\mathrm{M(L)}(\mu_{1,5}\text{-dca})(\mathrm{dca})]_n$ [M = Co (**1**), Ni (**2**); L = (N,N-diethyl,N′-(pyridin-2-yl)benzylidene)ethane-1,2-diamine; dca = dicyanamide] are isolated through single-pot reactions of a 1:1:2 M ratio of $\mathrm{M(OAc)_2 \cdot 4H_2O}$, L and Na(dca) in MeOH solution at room temperature and characterized on the basis of microanalyses, spectroscopic, thermal and other physicochemical results. X-ray structural study reveals that each metal(II) center in both compounds adopts a distorted octahedral geometry with an $\mathrm{MN_6}$ chromophore coordinated by three N atoms of the tridentate Schiff base (L) and three nitrile N atoms of one terminal and two single $\mu_{1,5}$ bridged dca units in a meridional alignment; each $\mu_{1,5}$ bridged dca unit connects other neighboring metal centers in a non-ending fashion affording a 1D chain. Variable-temperature magnetic susceptibility measurements of **1** and **2** show weak antiferromagnetic interactions among the metal centers through $\mu_{1,5}$ dca bridges.

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1. Introduction

The investigation on multidimensional coordination polymers of paramagnetic metal ions such as cobalt(II) [1–5] and nickel(II) [1,2,6–10] continues unabated because of their interesting structural and magnetic features. One-pot synthesis [11] of the metal ions, organic spacers and suitable bridging units is an efficient approach to prepare such coordination molecules. Schiff bases [12] are used as organic spacers because of their ease of preparation, structural variety, varied denticity and subtle steric and/or electronic effects controlling formation of coordination compounds differing in coordination numbers, nuclearities, and molecular and crystalline architectures. Dicyanamide (dca), a larger sized pseudohalide molecular ion-rod, is under active consideration as a bridging ligand because of its versatile coordination motifs [13] such as $\mu_{1,3}$-, $\mu_{1,5}$-, $\mu_{1,3,5}$-, $\mu_{1,1,3,5}$- and $\mu_{1,1,3,5,5}$ for the isolation of coordination polymers and polymer-based supramolecular entities that exhibit rich diversity in magnetic behaviors [14–26] including ferromagnetism, antiferromagnetism, canted-spin antiferromagnetism, weak canted-spin ferromagnetism, spin crossover (SCO), long range magnetic ordering, etc. We are also active in this field [22–25] and recently, we have reported a 1D cobalt(II) coordination polymer [26] in combination with a tetradentate Schiff base that shows interesting symmetry breaking SCO behavior. In our present endeavor, we have examined the coordination behavior of dca in combination with two different paramagnetic metal ions viz. cobalt(II) and nickel(II) using a tridentate N-donor Schiff base, (N,N-diethyl,N′-(pyridin-2-yl)benzylidene)ethane-1,2-diamine (L, Scheme 1) as organic spacer. Successfully, we have prepared two hexacoordinated iso-structural one-dimensional coordination polymers of the type $[M(L)(\mu_{1,5}\text{-dca})(dca)]_n$ [M = Co (**1**) and Ni (**2**)]. The syntheses, crystal structures, thermal and magnetic properties of these compounds are described in this paper.

2. Experimental

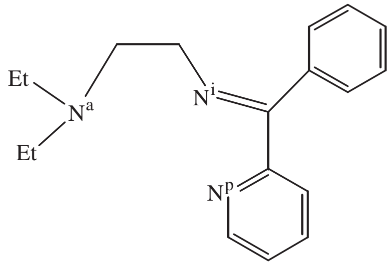
2.1. General remarks and physical measurements

2.1.1. Materials

High purity 2-benzoylpyridine (Lancaster, UK), N,N-diethylethane-1,2-diamine (SRL, India), sodium dicyanamide (Lancaster, UK) and metal(II) acetate tetrahydrate (M = Co and Ni) (E. Merck, India) were purchased from respective concerns and used as received. The Schiff base, (N,N-diethyl,N′-(pyridin-2-yl)benzylidine)ethane-1,2-diamine (L), was prepared by condensation of a 1:1 M ratio of 2-benzoylpyridine and N,N-diethylethane-1,2-diamine using a reported method [27]. All other chemicals and solvents used were AR grade. The synthetic reactions and work-up were done in open air.

2.1.2. Physical measurements

Elemental analyses (carbon, hydrogen and nitrogen) were performed on a Perkin–Elmer 2400 CHNS/O elemental analyzer. IR spectra (KBr discs, 4000–400 cm^{-1}) were recorded using a Perkin–Elmer FTIR model RX1 spectrometer. Ground state absorptions (in DMF) were measured with a Shimadzu model UV-2450 UV–vis spectrophotometer. Thermal behaviors were investigated with a Perkin–Elmer Diamond TG/DT analyzer heated from 40–700 °C under nitrogen. Magnetic measurements were carried out in the "Servei de Mesures Magnètiques" (Universitat de Barcelona) on polycrystalline samples (30 mg) with a Quantum Design SQUID MPMS-XL magnetometer working in the 2–300 K range. The sample was introduced into a standard plastic capsule with the background sample subtracted, taking into account the weight of the capsule. The magnetic fields were 0.1 T (for **1**) and 0.7 T (for **2**). The diamagnetic corrections were evaluated from Pascal's constants.



Scheme 1. (N^a,N^i,N^p) donor set in L.

2.2. Preparation of the complexes $[Co(L)(\mu_{1,5}\text{-dca})(dca)]_n$ (**1**) and $[Ni(L)(\mu_{1,5}\text{-dca})(dca)]_n$ (**2**)

A light yellow methanolic solution (15 ml) of L (0.281 g, 1 mmol) was added dropwise to a solution of $Co(OAc)_2{\cdot}4H_2O$ (0.249 g, 1 mmol) in the same solvent (15 ml). Na(dca) (0.178 g, 2 mmol) dissolved in MeOH (10 ml) was added slowly to it. The final reddish orange solution was filtered and the supernatant liquid was kept undisturbed in open air for slow evaporation. After a week deep red crystalline product of **1** was isolated by filtration, washed with dehydrated alcohol and dried *in vacuo* over silica gel. Yield: 0.354 g (75%). For preparation of **2** in pure crystalline state, similar reaction condition and reaction stoichiometry as used in **1** were used except that $Ni(OAc)_2{\cdot}4H_2O$ (0.248 g, 1 mmol) instead of $Co(OAc)_2{\cdot}4H_2O$ was used. The light green solution was processed as in **1** to isolate faint-green crystals of pure **2**. Yield: 0.377 g (80%). Anal. Calc. for $C_{22}H_{23}N_9Co$ (**1**): C, 55.9; H, 4.9; N, 26.6. Found: C, 55.7; H, 4.7; N, 26.7%. IR (KBr, cm^{-1}): 2306 (w), 2282 (m), 2250 (m), 2230 (m), 2184 (s), 2165 (s), 1636 (m), 1592 (m), 1366 (m), 1342 (m), 935 (m), 919 (m). UV–Vis (DMF, λ_{max}/nm): 514, 274. Anal. calcd. for $C_{22}H_{23}N_9Ni$ (**2**): C, 55.9; H, 4.9; N, 26.6. Found: C, 55.8; H, 4.8; N, 26.5%. IR (KBr, cm^{-1}): 2309 (w), 2284 (m), 2254 (m), 2229 (m), 2182 (s), 2167 (s), 1639 (m), 1595 (m), 1370 (m), 1338 (m), 936 (w), 917 (w). UV–Vis (DMF, λ_{max}/nm): 762, 599, 325, 277.

2.3. X-ray crystallographic analyses

Single crystals of **1** and **2** suitable for X-ray analyses were selected from those obtained by open evaporation of methanolic solutions of the reaction mixtures at 298 K. Crystallographic data were collected on a Bruker AXS SMART APEX II diffractometer using graphite monochromated Mo Kα radiation (λ = 0.71073 Å) at 295(2) K. The detector frames were integrated by use of the program SAINT [28] and absorption corrections were performed with SADABS [29]. Of the 43756 (for **1**) and 22851 (for **2**) total reflections for the complexes, 5982 (for **1**) and 5896 (for **2**) with $[I > 2\sigma(I)]$ were used for structures solutions. The structures were solved by direct methods using SHELXTL [30]. All non-hydrogen atoms were refined with anisotropic displacement parameters whereas hydrogen atoms were placed in calculated positions where possible and given isotropic U values 1.2 times that of the atom to which they are bonded. The final differences Fourier map showed the maximum and minimum peak heights at 0.476 and −0.274 $eÅ^{-3}$ for **1** and 0.412 and −0.316 $eÅ^{-3}$ for **2** with no chemical significance. Materials for publication were prepared using SHELXTL, PLATON [31] and ORTEP-32 [32] programs. A summary of the crystallographic data and structure determination parameters of **1** and **2** are given in Table 1.