Nickel(II)dicyanamide complexes containing a diamine as end-capping ligand: Composition tailored architectures and magnetic properties

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ABSTRACT

One 0D monomer *trans*-[Ni(pn)$_2$(dca)$_2$] (**1**), one neutral 2D polymer [Ni(pn)(dca)$_2$]$_n$ (**2**) and one polycationic 1D polymer [Ni(pn)$_2$(dca)]$_n$(PF$_6$)$_n$ (**3**) (pn = 1,3-propanediamine; dca = dicyanamide) have been synthesized and X-ray crystallographically characterized. **1** has terminal *trans*-Ni(dca)$_2$ unit, **2** contains both double bridged Ni–(NCNCN)$_2$–Ni and single bridged Ni–(NCNCN)–Ni units in alternate fashion and **3** consists of single Ni–(NCNCN)–Ni bridge by covalent bonds. The nickel(II) centers are six-coordinated with distorted octahedral geometry. Multiple lateral N–H⋯N, C–H⋯N, N–H⋯F and C–H⋯F hydrogen bondings promote dimensionality. Variable-temperature magnetic measurements indicate weak antiferromagnetic interactions through $\mu_{1,5}$ bridge(s).

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1. Introduction

The design and construction [1,2] of metal–organic coordination frameworks are extensively studied for the preparation of functional materials [3–7] of different shapes and sizes [8] through control and manipulation of strong metal ligand covalent bonds [9,10] along with non-covalent bonds like weak hydrogen bondings [11–13] which is a general protocol in supramolecular chemistry [14,15]. Judicious choice [16] of organic blockers with varied denticities, efficient polyatomic bridging units with multiple connectors and metal ion templates with malleable coordination spheres give rise to veritable molecular and crystalline architectures [15,17]. Self-assembly [18] of the building components is an efficient approach to construct such frameworks. Pseudohalides like azide, thiocyanate and cyanate [19–22] have long been known for their versatile coordination motifs leading to different 1D, 2D and 3D coordination polymers and polymer-based supramolecular entities. Dicyanamide (dca) [23], a larger pseudohalide molecular-ion rod, is now under active consideration [24–28] by the coordination chemists for its exciting coordination modes and related properties. Recently, we are actively engaged [29–34] in the preparation of functional polymers and polymer-based supramolecular

units through variations of ligand backbones and metal ion coordination environments using azide, thiocyanate and cyanate as bridges/terminals. The investigation of mono-, di- and polynuclear complexes of nickel(II) is an important objective because of their interesting magnetic properties [35–38]. This work stems from our interests to prepare different coordination polymers and polymer-based supramolecular entities of nickel(II)dicyanamides in combination with an α,ω-diamine like 1,3-propanediamine (pn). Cursory report of a 1D polymer of the type [Ni(pn)$_2$(dca)]$_n$(ClO$_4$)$_n$ has been made by Dong et al [39]. Here we have made a systematic research on nickel(II)dicyanamide containing pn as an end-capping ligand. Successfully, we have isolated one mononuclear compound *trans*-[Ni(pn)$_2$(dca)$_2$] (**1**) and two polynuclear compounds of the types [Ni(pn)(dca)$_2$]$_n$ (**2**) and [Ni(pn)$_2$(dca)]$_n$(PF$_6$)$_n$ (**3**) along with the reported compound [Ni(pn)$_2$(dca)]$_n$(ClO$_4$)$_n$ using different nickel(II) salts and with varied mole ratios of nickel(II), pn, dca and appropriate counter anions. The details of syntheses, characterizations, X-ray structures and magnetic properties of these complexes are described below.

2. Experimental

2.1. Materials and methods

High purity 1,3-propanediamine (Spectrochem, India), sodium dicyanamide (Lancaster, UK), nickel(II) chloride/nitrate/acetate

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(E. Merck, India), sodium perchlorate (Lancaster, UK) and potassium hexafluorophosphate (Fluka, Germany) were purchased from respective concerns and used as received. Nickel(II) perchlorate hexahydrate was prepared [40] by treatment of the corresponding nickel(II) carbonate (E. Merck, India) with perchloric acid (E. Merck, India) followed by slow evaporation on a steam-bath, filtration through a fine glass-frit, and preserved in a desiccator containing concentrated sulfuric acid (E. Merck, India) for subsequent uses. All other chemicals and solvents were AR grade and used as received. The synthetic reactions and work-up were done in open air.

Caution! Perchlorate compounds of metal ions are potentially explosive [41] especially in the presence of organic ligands. Only a small amount of these materials should be prepared and handled with care.

2.2. Physical measurements

Elemental analyses (carbon, hydrogen and nitrogen) were performed on a Perkin–Elmer 2400 CHNS/O elemental analyzer. IR spectra (KBr discs, 4000–300 cm^{-1}) were recorded using a Perkin–Elmer FTIR model RX1 spectrometer. UV–Vis (in DMF) and reflectance spectra were measured with a Jasco model V-570 UV–Vis-NIR spectrophotometer. The temperature dependence of magnetic susceptibilities was measured on polycrystalline samples with a Quantum Design MPMS XL-5 SQUID magnetometer operating at a magnetic field of 0.05, 0.2, 1 Tesla (for **2**) and 0.1 Tesla (for **1** and **3**) over a temperature range 2–300 K. The diamagnetic corrections were evaluated from Pascal's constants.

2.3. Preparation of the complexes

Mononuclear **1** was prepared from chloride, nitrate and acetate salts of nickel(II) using a 1:2:2 molar ratio of metal salts, bidentate diamine (pn) and dicyanamide (dca). The neutral polymer **2** was obtained using a 1:1:2 ratio of any of those nickel(II) salts, pn and dca. Using nickel(II) perchlorate, these 1:2:2 and 1:1:2 of the metal ion, blocking ligand and bridging unit invariably resulted in reported [39] polycationic polymer [Ni(pn)$_2$(dca)]$_n$(ClO$_4$)$_n$ albeit in lower yields; extraneous addition of KPF$_6$ into the solution mixtures afforded [Ni(pn)$_2$(dca)]$_n$(PF$_6$)$_n$ (**3**) once again in lower yields. However, direct addition of NaClO$_4$/KPF$_6$ to a 1:2:1 molar ratio of nickel(II) chloride/nitrate/acetate results in [Ni(pn)$_2$(dca)]$_n$(ClO$_4$)$_n$/[Ni(pn)$_2$(dca)]$_n$(PF$_6$)$_n$ (**3**) in better yield. The typical syntheses are described below.

2.3.1. [Ni(pn)$_2$(dca)$_2$] (1)
An aqueous solution (5 ml) of pn (148.0 mg, 2 mmol) was added dropwise to a solution of NiCl$_2$·6H$_2$O (237.7 mg, 1 mmol) in the same solvent (10 ml) followed by NaN(CN)$_2$ (178.0 mg, 2 mmol) in water (10 ml). The blue-violet solution was filtered and kept undisturbed in an open air for evaporation. Within a week deep blue-violet rectangular crystals of **1** that resulted were collected, washed with hexane and dried *in vacuo* over silica gel indicator. Yield: 278.1 mg (82%). *Anal.* Calc. for C$_{10}$H$_{20}$N$_{10}$Ni (**1**): C, 35.4; H, 5.9; N, 41.5. Found: C, 35.1; H, 5.7; N, 41.1%. IR (KBr, cm^{-1}): v(N–H) 3290, 3240; v(C–H) 2970, 2930; $v_{as} + v_s$(C≡N) 2362, 2274; v_{as}(C≡N) 2226; v_s(C≡N) 2164; v_{as}(C–N) 1360, 1318; v_s(C–N) 902. UV–Vis (λ_{max}, nm): 572, 359, 267.

2.3.2. [Ni(pn)(dca)$_2$]$_n$ (2)
To an aqueous solution (10 ml) of NiCl$_2$·6H$_2$O (237.7 mg, 1 mmol), a solution of pn (74.2 mg, 1 mmol) in the same solvent (5 ml) was added dropwise in a glass beaker followed by an aqueous solution (10 ml) of NaN(CN)$_2$ (178.0 mg, 2 mmol) resulting a deep blue solution. This was filtered and kept undisturbed in an open air for evaporation. After two weeks blue plate-like crystals

of **2** were separated, which were filtered, washed with hexane and dried *in vacuo* over silica gel indicator. Yield: 211.9 mg (80%). *Anal.* Calc. for C$_7$H$_{10}$N$_8$Ni (**2**): C, 31.7; H, 3.8; N, 42.5. Found: C, 31.5; H, 3.8; N, 42.3%. IR (KBr, cm^{-1}): v(N–H) 3292, 3242; v(C–H) 2978, 2932; $v_{as} + v_s$(C≡N) 2286; v_{as}(C≡N) 2252; v_s(C≡N) 2187; v_{as}(C–N) 1362, 1316; v_s(C–N) 900. UV–Vis (λ_{max}, nm): 616, 376, 267.

2.3.3. [Ni(pn)$_2$(dca)]$_n$(PF$_6$)$_n$ (3)
2.3.3.1. *Method A.* To a solution (10 ml) of NiCl$_2$·6H$_2$O (237.7 mg, 1 mmol) in water (10 ml), pn (148.4 mg, 2 mmol) in water (10 ml) and NaN(CN)$_2$ (89.2 mg, 1 mmol) in the same solvent (5 ml) was added slowly in succession. Finally, an aqueous solution (5 ml) of KPF$_6$ (184.1 mg, 1 mmol) was added to the resulting blue-violet reaction mixture and left undisturbed in an open air for evaporation. After ten days blue-violet microcrystals of **3** were collected and dried in *vacuo* over silica gel indicator. Yield: 326.0 mg (78%).

2.3.3.2. *Method B.* Aqueous solution (10 ml) of KPF$_6$ (368.1 mg, 2 mmol) was added to a solution (10 ml) of Ni(ClO$_4$)$_2$·6H$_2$O (365.7 mg, 1 mmol) in the same solvent and stirred magnetically for 15 min; pn (148.4 mg, 2 mmol) in 10 ml water and dca (89.2 mg, 1 mmol) in same amount of the solvent were added successively to the metal salt solution. The light blue-violet solution was processed as in Method A to get rectangular shiny microcrystals of **3**. Yield: 313.5 mg (75%).

2.3.3.3. *Method C.* **3** was also prepared by metathesis of [Ni(pn)$_2$(dca)]$_n$(ClO$_4$)$_n$ and KPF$_6$. The former was isolated (yield, 80%) using a 1:2:1 molar ratio of Ni(ClO$_4$)$_2$·6H$_2$O, pn and dca – an improved stoichiometry over Dong et al in which a 1:1:2 molar ratio [39] of the building components was used (yield not reported). A 1:1 ratio of [Ni(pn)$_2$(dca)]$_n$(ClO$_4$)$_n$ and KPF$_6$ in DMF–water solvent mixture (1:3) was kept in open air for evaporation. Blue-violet shiny crystals of **3** were obtained (yield, 80%) within a week and were isolated as described in Method A.

The microanalytical and spectroscopic results for **3** obtained from methods A to C are akin which are listed here. *Anal.* Calc. for C$_8$H$_{20}$N$_7$F$_6$PNi (**3**): C, 23.0; H, 4.8; N, 23.6. Found: C, 22.8; H, 4.7; N, 23.4%. IR (KBr, cm^{-1}): v(N–H) 3289, 3245; v(C–H) 2973, 2933; $v_{as} + v_s$(C≡N) 2283; v_{as}(C≡N) 2244; v_s(C≡N) 2176; v_{as}(C–N) 1355, 1315; v_s(C–N) 903; v(PF$_6$) 851, 838, 559. UV–Vis (λ_{max}, nm): 574, 359, 267.

2.4. X-ray crystallographic analyses

Single crystals of **1**–**3** and [Ni(pn)$_2$(dca)]$_n$(ClO$_4$)$_n$ suitable for X-ray analyses were selected from those obtained by open evaporation of aqueous solutions of the reaction mixtures at 298 K. Crystallographic data were collected on a Bruker APEXII CCD area detector diffractometer [42] using graphite monochromated Mo Kα radiation (λ = 0.71073 Å) at 100 K with the Oxford Cryosystem Cobra low temperature attachment. The collected data were reduced using SAINT [42] and the empirical absorption corrections were performed using SADABS program [42]. A summary of the crystallographic data and structure determination parameters of **1**–**3** is given in Table 1 and [Ni(pn)$_2$(dca)]$_n$(ClO$_4$)$_n$ as Supplementary material. Of 9378, 19 111 and 43 722 collected reflections, 1974, 4249 and 7144 unique reflections were recorded for **1**, **2** and **3**, respectively. The structures were solved by direct methods using SHELXTL [43]. All non–Hydrogen atoms were refined anisotropically, whereas the H atoms attached to N were located in difference maps and isotropically refined and the remaining H atoms were placed in calculated positions with the C–H distance of 0.97 Å after checking their positions in the difference map. The U_{iso} values were