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New 3D dicyanamide bridged coordination polymer of Ni(II): Synthesis, crystal structure, magnetic properties and antibacterial assay

Leila Tabrizi [a], Hossein Chiniforoshan [a,*], João P. Araújo [b], Armandina M.L. Lopes [b,c], Helmar Görls [d], Winfried Plass [d], Gholamhossein Mohammadnezhad [a]

[a] *Department of Chemistry, Isfahan University of Technology, Isfahan 84156-83111, Iran*
[b] *Department of Physics, and Astronomy, IFIMUP-IN, FUCP, University of Porto, 4169-007 Porto, Portugal*
[c] *Center of Nuclear Physics, University of Lisbon, 1649-003 Lisbon, Portugal*
[d] *Institut für Anorganische und Analytische Chemie, Lehrstuhl für Anorganische Chemie II, Friedrich-Schiller-Universität Jena, Humboldtstr. 8, 07743 Jena, Germany*

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ABSTRACT

One new coordination polymer of Ni(II), $\{[\mathrm{Ni}(\mu_{1,5}\text{-dca})_2(\mu\text{-hmt})]\mathrm{H_2O}\}_n$, (**1**), using hmt (hmt = hexamethylenetetramine), and dca (dca = dicyanamide) as bridged ligands has been synthesized and characterized by X-ray single crystal analysis. Compound **1** is a three-dimensional polymer which contains the solvent water molecules. Both dca and hmt are μ_2-bridged. In addition; thermal stability of **1** is investigated by thermogravimetric (TGA) analysis. Antibacterial activities of complex **1** also show greater activity than the reference antibiotic gentamycin against *Klebsiella pneumonia*. Magnetic susceptibility measurements revealed weak antiferromagnetic exchange interactions between the nickel centers bridged by long hmt and dicyanamides ligands. A 3D long-range magnetic order is observed below 22 K with a small ferromagnetic component, possibly due to spin canting developing at these low temperatures.

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1. Introduction

The design of multidimensional networks is highly influenced by the judicious choice of ligand, metal coordination geometry, template, and other subtle factors, such as counter ion, solvent choice and reaction temperature [1–7]. Metal dicyanamide (dca) coordination polymers constitute a hot subject of research, due to their rich structural and topological features along with the magnetic properties related to this ligand [8]. Dicyanamide may act as a bidentate bridging ligand by coordinating to two different metal centers through its two terminal N (nitrile) atoms, or as a tridentate bridging ligand with additional coordination through the middle N(amide) atom (Scheme 1) [9–11]. When there is another ancillary ligand, L (L being monodentate or Lewis bases such as pyridine, 2,2′-bipyridine, 4,4′-bipyridine, 4-cyanopyridine, 1,2-bis(4-pyridyl)ethane, etc.), the magnetic behavior is directly related to either the coexistence of the $\mu_{1,3}$- and $\mu_{1,5}$-dca pathways [12–14] or the spatial dimensionality of the crystal structure due to the existence of another bridging ligand [15–18].

Generally, the coupling between $\mu_{1,5}$-dca bridges is antiferromagnetic, but in some very special cases ferromagnetic coupling has also been reported [19,20]. It is worth mentioning that, recently, in a one-dimensional $\mu_{1,5}$-dca copper(II) complex the ferromagnetic coupling has been assigned to be due to the π–π contacts of the aromatic chelated rings rather than the $\mu_{1,5}$-dca bridges [21].

The use of hexamethylenetetramine (hmt), also known as hexamine or urotropine, a simple heterocyclic compound with a cage-like structure, has also been investigated and a considerable number of hmt-driven metal–organic networks have been reported in the last few years. With regard to coordination chemistry, hmt is a versatile ligand capable of adopting different coordination modes that span from the terminal monodentate to bridging bi-, tri- and tetradentate modes [22]. In addition, due to the good H-bond accepting behavior, hmt is very often trapped by metal–organic compounds forming various molecular adducts and supramolecular structures [23–28]. Also, hmt polymers attracts significant attention due to the diverse practical applications of such compounds in fields ranging from molecular magnetism, biological activities and gas storage to photoluminescence and catalysis [29–31]. These interesting properties of dca complexes prompted us to prepare one new dca bridged 3D polymeric network $\{[\mathrm{Ni}(\mu_{1,5}\text{-dca})_2(\mu\text{-hmt})]\mathrm{H_2O}\}_n$ (**1**) which used hmt as coligand. Herein, we report the synthesis, crystal structure, magnetic properties, antibacterial activity and thermal properties of this compound.

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* Corresponding author. Tel.: +98 3133913261; fax: +98 3133912350.
E-mail address: Chinif@cc.iut.ac.ir (H. Chiniforoshan).

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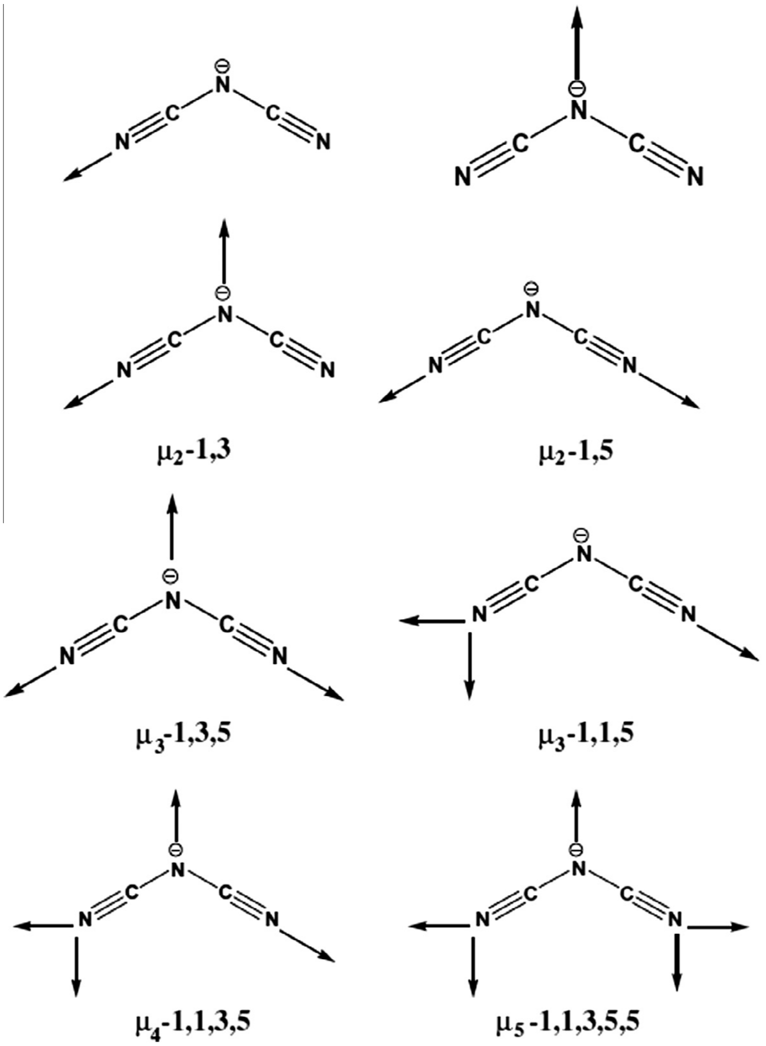

Scheme 1. Different bridging modes of dicyanamide ligand.

2. Experimental

2.1. Materials

All the chemicals and solvents were purchased from Merck or Sigma–Aldrich compounds and were used without any further purification.

2.2. Physical measurements

Fourier transform infrared spectra were recorded on a FT-IR JASCO 680-PLUS spectrometer in the region of 4000–400 cm^{-1} using KBr pellets. UV–Vis spectra were recorded as Nujol mulls and in solution on a JASCO 7580 UV–Vis–NIR double-beam spectrophotometer using a quartz cell with a path length of 10 mm. Elemental analyses were performed by using a Leco, CHNS-932elemental analyzer. Thermogravimetric (TGA) analyses were performed under Argon using STA-503 at a heating rate of 10 °C/min. The temperature dependent magnetic susceptibility χ (=M/H) measurements, performed between 5 and 320 K under a $H = 50$ Oe magnetic field (taking into account the coil remnant field and earth field compensation), were acquired on samples using a commercial (Quantum Design) superconducting quantum interference device (SQUID) magnetometer. The measurements were performed using the zero field cooling (ZFC) and field cooling (FC) procedures. Isothermal magnetization between 4.5 and 25 K was acquired while sweeping the magnetic field from 5.5 down to 0 T.

2.3. Synthesis of $\{[Ni(\mu_{1,5}\text{-}dca)_2(\mu\text{-}hmt)]H_2O\}_n$ (**1**)

To the solution of $Ni(OAc)_2{\cdot}4H_2O$ (24.9 mg, 0.1 mmol), in 20 cm^3 methanol, added aqueous solution (5 cm^3) of hmt (14 mg, 0.1 mmol) followed by the addition of a solution of sodium dicyanamide (17.8 mg, 0.2 mmol) in 5 cm^3 water into the mixture with continuous stirring. The mixture was stirred for 60 min. at room temperature, and then filtered. The resulting solution was kept at room temperature. After a few days, shiny blue single crystals suitable for X-ray determination were obtained (Yield 54%).

Elemental analysis and results of AAS were in good agreement with the $C_{10}H_{14}N_{10}NiO$ stoichiometry for **1**. Found (Calc. %): Ni, 16.74 (16.82); C, 34.36 (34.42); N, 40.05 (40.14); H, 3.39 (4.04). IR data on KBr (ν, cm^{-1}) pellets: 3400 m ν(O–H); 2333s $\nu_s + \nu_{as}$(C≡N); 2252s ν_{as}(C≡N); 2197s ν_s(C≡N); 1391 ν_{as}(C–N)(dca); 1248s, 1222w ν(C–N)(hmt); 996ν_s(C–N), 825 $\rho(CH_2)$ [32]. UV–Vis–NIR: λ/nm as Nujol mull: 498, 651 and 1040 (see Supplementary information Fig. S1); in DMSO: 504 nm ($\varepsilon \approx 64$ L mol^{-1} cm^{-1}), 658 nm ($\varepsilon \approx 36$ L mol^{-1} cm^{-1}), 1036 nm ($\varepsilon \approx 46$ L mol^{-1} cm^{-1}) which assigned to $^3A_2g \rightarrow {}^3T_1g$ (P), $^3A_2g \rightarrow {}^3T_1g$ (F) and $^3A_2g \rightarrow {}^3T_2g$, respectively (Fig. 1) [33], suggesting that complex **1** retains its structure in solution.

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