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Two new Ni^{II} complexes with $\mu_{1,5}$-dicyanamide as bridging ligand

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Abstract

One 3D and one 2D $\mu_{1,5}$-dicyanamide bridged Ni^{II} complexes having molecular formula $[Ni(L1)(dca)_2]$ (**1**) and $[Ni_2(L2)_2(dca)_4] \cdot 0.5H_2O$ (**2**) (L1 = 4-(2-aminoethyl)-morpholine, L2 = 1-(2-aminoethyl)-piperidine and dca = dicyanamide dianion) have been synthesized. X-ray single crystal analyses and low temperature magnetic measurements were used to characterize the complexes. Complex **1** represents a 3D structure where each metal ion is chelated by morpholine ligand (L1) and connected by four $\mu_{1,5}$-dca. Whereas complex **2** shows an undulated 2D structure with grid of (4,4) topology having two crystallographically independent Ni^{II} centers in similar octahedral environment where each metal center is chelated by one piperidine ligand (L2) and coordinated by four $\mu_{1,5}$-dca. Magnetic measurements of both the complexes indicate weak antiferromagnetic interactions through the μ-$_{1,5}$-dca bridging ligands.

Keywords: Ni(II); Dicyanamide; Crystal structure; Magnetic study

1. Introduction

Multidimensional coordination polymers consisting of transition metal cations are under intense investigation in the context of molecule-based magnets. One common strategy for the synthesis is to employ transition metal ions as source of magnetic moment and connect the metal ions through proper bridging ligands for providing superexchange interaction. Including dicyanamide [1–11], a large number of bridging ligands such as azide [12], dicarboxylate [13], and cyanide [14] have been employed for the construction of multidimensional molecular architectures where they also behave as good candidate for superexchange interaction. Here, we have selected dicyanamide (dca) having three N-donor sites, showing versatility in coordination modes [5] (Scheme 1: (a) terminal, (b) bridging bidentate, (c) three-coordinated, where all of its nitrogens behave as monocoordinated and (d) unusual μ_4-dca, where dca acts as tetra-coordinated, with one of the terminal nitrogens acting as bicoordinated) towards metal ions that plays an important role for the construction of multidimensional molecular architectures.

Series of dicyanamide bridged complexes of formula α-$[M(dca)_2]$ have a 3D rutile-like single net structure and display interesting magnetic behavior [1–5]. Significantly, three-coordinate dca (μ_3-dca + $\mu_{1,5}$-dca) is present in all of these structures, allowing access to M–NCN–M magnetic exchange pathways and thereby the magnetic order is likely generated in all cases from this three-atom pathway of μ_3-dca ligand [1–5].

Similarly, when there is another ancillary ligand, L (L being monodentate or chelated Lewis bases such as py, 2,2′-bpy, 4,4′-bpy, pyrazine, 4CN-py, 1,2-bis(4-pyridyl)ethane, etc.), the magnetic behavior is directly

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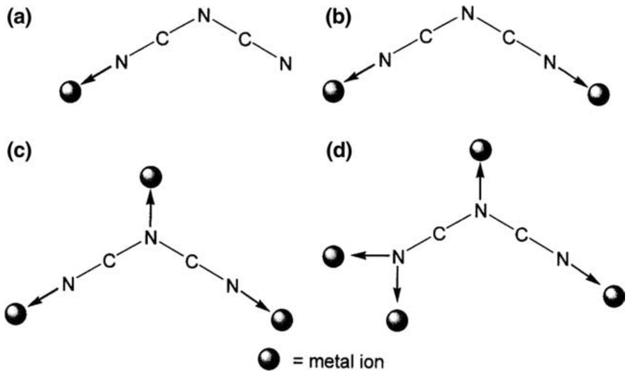


Scheme 1.

related to either the coexistence of the $\mu_{1,3}$- and $\mu_{1,5}$-dca pathways [8] or the spatial dimensionality of the crystal structure due to the existence of another bridging ligand [9].

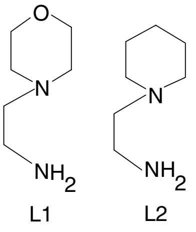
Generally, the coupling between $\mu_{1,5}$-dca bridges is antiferromagnetic [1–9], but in some very special cases ferromagnetic coupling has also been reported [10]. It is worth mentioning that, very recently, in a one-dimensional $\mu_{1,5}$-dca copper(II) complex the ferromagnetic coupling has been assigned to be due to the π–π contacts of the aromatic chelated rings rather than the $\mu_{1,5}$-dca bridges [11].

In this paper, two new complexes [Ni(L1)(dca)$_2$] (**1**) and [Ni$_2$(L2)$_2$(dca)$_4$] · H$_2$O (**2**) (L1 = 4-(2-aminoethyl)-morpholine, L2 = 1-(2-aminoethyl)-piperidine, Scheme 2) have been prepared and characterized. In both the complexes, L acts as chelated ligand, having each Ni^{II} ion four μ-$_{1,5}$-dca bridging ligands to build the net.

2. Experimental

2.1. Materials

High purity Ni(NO$_3$)$_2$ · 6H$_2$O (98%), 4-(2-aminoethyl)-morpholine (99%), 1-(2-aminoethyl)-piperidine (99%) and sodium dicyanamide (96%) were purchased from Aldrich and were used as received. All other chemicals were of AR grade.



Scheme 2.

2.2. Physical measurements

Elemental analyses (carbon, hydrogen and nitrogen) were performed using a Perkin–Elmer 240C elemental analyzer. IR spectra were measured from KBr pellets on a Nicolet 520 FTIR spectrometer. The magnetic behavior was measured on a SQUID susceptometer (QUANTUM-DESIGN MPMS XL-5) in the temperature range of 2–300 K and varying the magnetic field range. Magnetization measurements were made in the same SQUID at 2 K. Diamagnetic corrections were estimated from Pascal's table [15].

2.3. Synthesis

2.3.1. Complex **1**

4-(2-aminoethyl)-morpholine (1 mmol, 0.131 ml) was added drop wise to a solution (~10 ml) of Ni(NO$_3$)$_2$ · 6-H$_2$O(1 mmol, 0.291 mg) in H$_2$O-CH$_3$CN(2:1). To this light green solution, an aqueous solution (~7 ml) of dicyanamide (2 mmol, 0.178 mg) was added slowly. After one hour stirring, a greenish compound was separated out, which was filtered off and the filtrate was kept in a CaCl$_2$ desiccator. After a few days, shining green complex was separated out. Single crystals for X-ray analysis were obtained on recrystallizing the green complex from hot water. Yield: 76%. *Anal.* Calc. for C$_{10}$H$_{14}$N$_8$NiO: C, 37.38; H, 4.36; N, 34.89. Found: C, 37.46; H, 4.29; N, 35.01%. IR spectra: 2304(s), 2258(w), 2183(vs), 1596(vw), 1373(w), 1336(w), 1113(w), 1070(w) cm^{-1}.

2.3.2. Complex **2**

It has also been synthesized following the same reaction procedure as adopted in **1**. Here, 1-(2-aminoethyl)-piperidine (1 mmol, 0.143 ml) was added drop wise instead of 4-(2-aminoethyl)-morpholine. A blue compound was separated out, which was filtered and the blue filtrate was kept in a CaCl$_2$ desiccator. After a few days, a deep blue crystalline complex was found. The single crystals suitable for X-ray analysis were obtained on recrystallizing the blue complex from H$_2$O–MeOH (1:1) mixture. Yield 72%. *Anal.* Calc. for C$_{22}$H$_{33}$N$_{16}$Ni$_2$O$_{0.5}$(%): C, 40.86; H, 5.10; N, 34.67. Found: C, 40.71; H, 4.89; N, 33.72%. IR spectra: 2949–3346(w), 2299(vs), 2256(s), 2190(vs), 2163(vs), 1604(w), 1384(m), 1350(s), 1077(m) cm^{-1}.

2.4. Crystallographic data collection and refinement

Details for the structure determinations are given in Table 1. Intensity data were collected with Mo Kα radiation using the MAR-research Image Plate System. The crystals were positioned at 70 mm from the Image Plate. 100 frames were measured at 2° intervals with a counting time of 2 min. Data analysis was carried out with the XDS program [16]. The structures were solved using