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Inorganica Chimica Acta 359 (2006) 1395–1403
Inorganica Chimica Acta
www.elsevier.com/locate/ica

Synthesis, crystal structure, magnetic behavior and thermal property of three polynuclear complexes: $[M(dca)_2(H_2O)_2]_n \cdot (hmt)_n$ [M = Mn(II), Co(II)] and $[Co(dca)_2(bpds)]_n$ [dca, dicyanamide; hmt, hexamethylenetetramine; bpds, 4,4′-bipyridyl disulfide]

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Received 22 August 2005; accepted 16 September 2005
Available online 2 November 2005

Abstract

Three $\mu_{1,5}$-dicyanamide bridged Mn(II) and Co(II) complexes having molecular formula $[Mn(dca)_2(H_2O)_2]_n \cdot (hmt)_n$ (**1**), $[Co(dca)_2(H_2O)_2]_n \cdot (hmt)_n$ (**2**) and $[Co(dca)_2(bpds)]_n$ (**3**) [dca = dicyanamide; hmt = hexamethylenetetramine; bpds = 4,4′-bipyridyl disulfide] have been synthesized and characterized by single crystal X-ray diffraction study, low temperature (300–2 K) magnetic measurement and thermal behavior. The X-ray diffraction analysis of **1** and **2** reveals that they are isostructural, comprising of 1D coordination polymers $[M(dca)_2(H_2O)_2]_n$ [M = Mn(II), Co(II) for **1** and **2**, respectively] with uncoordinated hmt molecules located among the chains. The $[M(dca)_2(H_2O)_2]_n$ chains and the lattice hmt molecules are connected through H-bonds resulting in a 3D supramolecular architecture. The octahedral N_4O_2 chromophore surrounding the metal ion forms via two *trans* located water oxygens and four nitrogens from four nitrile dca. Complex **3** is a 1D chain formed by two $\mu_{1,5}$-dca and one bridging bpds. The octahedral N_6 coordination sphere surrounding the cobalt ions comprises four nitrogens from dca and two from bpds. Low temperature magnetic study indicates small antiferromagnetic coupling for all the complexes. Best fit parameters for **1**: $J = -0.17\ cm^{-1}$, $g = 2.03$ with $R = 6.1 \times 10^{-4}$; for **2**, $J = -0.50\ cm^{-1}$, and for **3**, $J = -0.95\ cm^{-1}$.

Keywords: Mn(II); Co(II); Dicyanamide; Crystal structure; Magnetic study

1. Introduction

Transition metal dicyanamide (dca) coordination polymers are of great interest in the current research due to their novel structural topology, originated from the versatile coordination modes of dca [1] (Scheme 1) leading to interesting magnetic properties [2]. Till date a large number of 1D, 2D and 3D coordination polymers have been reported. While synthesizing transition metal dicyanamide complexes, most commonly used strategies are: (i) combination of metal and dca only generating 2D sheet, β-$M(dca)_2$ [3], 3D rutile-type, α-$M(dca)_2$ [4], and 2D square networks of (4,4) topology, e.g., $(Ph_4X)[M(dca)_3]$ (X = P or As; M = Mn or Co) [5]; (ii) dca in combination with

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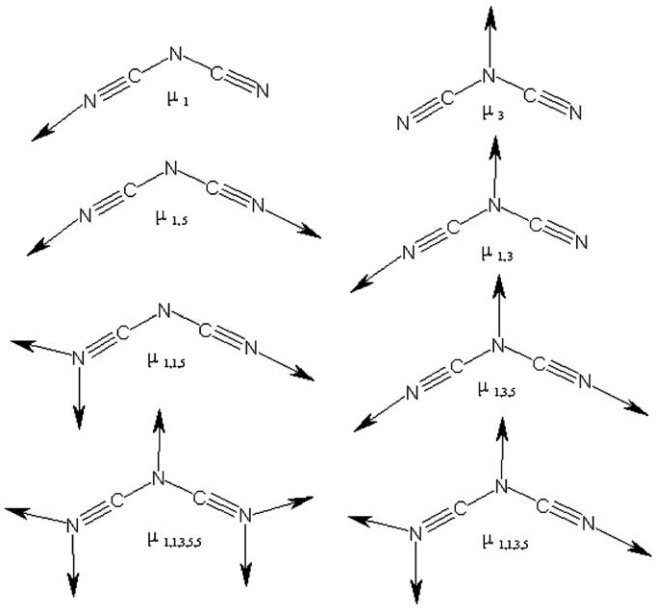
doi:10.1016/j.ica.2005.09.035



Scheme 1.

bi- or tridentate chelating ligands such as 2,2′-bipyridine; 1,10-phenanthroline; 2,2′-bipyrimidine; 2,2′-biimidazole; 1,2-bis-(diphenylphosphino)ethane; bis(2-pyridylcarbonyl)-amidate [2b,6]; (iii) dca in combination of bridging or terminal L ligand, $M(dca)_2(L)_n$ (L terminal = imidazole, pyridine, pyridine *N*-oxide, MeOH, EtOH, DMF [7] and bridging L ligand = 4,4′-bipyridine; *trans*-1,2-bis(4-pyridyl)ethylene; 1,2-bis-(4-pyridyl)ethane; 1,2-bis(4-pyridyl)-4,4,5,5-tetramethylimidazoline-1-oxyl; pyrazine; phenazine; pyrimidine; 4,4′-bipyridine *N*,*N*′-dioxide) [8]; (iv) anionic metal dicyanamide extended networks through cation templation, $[M'L][M(dca)_4]$ (M′ = Cu(II), M = Mn(II), Co(II); L = a tetradentate macrocyclic ligand) [9] and (v) $\mu_{1,5}$-dca complex with tetradentate macrocyclic ligand [10]. Thus, depending on the above mentioned combinations several novel structural topologies, along with interesting magnetic properties, have been studied. We have recently reported some novel observations utilizing dca in the synthesis of coordinately unsaturated Mn(II) centers [11]. Literature survey reveals the fact that polymeric networks of dca in combination with hexamethylenetetramine (hmt), commercially known as urotropin and 4,4′-bipyridyl disulfide (bpds), are rare. We have chosen hmt for its flexible μ_2 and μ_4 bridging modes [12], besides its behavior as monodentate ligand [13]. On the other hand, the choice of bpds was simulated based on the fact that dca and bpds can connect metal ions in double bridging fashion [7,8,14], as observed also for azide anions. In fact we have recently reported a Cu(II) framework containing singly bridged azide and doubly bridged bpds linkers [15].

Herein, we report the synthesis, crystal structure, low temperature magnetic study and thermal behavior of three transition metal dicyanamide complexes, namely $[Mn(dca)_2(H_2O)_2]_n \cdot (hmt)_n$ (**1**), $[Co(dca)_2(H_2O)_2]_n \cdot (hmt)_n$ (**2**) and $[Co(dca)_2(bpds)]_n$ (**3**).

2. Experimental

2.1. Materials

High purity $MnCl_2 \cdot 4H_2O$ (98%), sodium dicyanamide (96%), hexamethylenetetramine (99%) and 4,4′-bipyridyl disulfide (Aldrithiol-4; 98%) were purchased from Aldrich Chemical Co. Inc. and were used. All other chemicals were of AR grade.

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. Magnetic measurements were carried out on polycrystalline samples (20–30 mg) in the 'Servei de Magnetoquímica, Universitat de Barcelona' with a Quantum Design MPMS SQUID magnetometer operating at a magnetic field of 0.1 T within the temperature range 2–300 K. The diamagnetic corrections were evaluated from Pascal's constants. Thermogravimetric analyses were carried out on a Mettler Toledo Star system.

2.3. Synthesis

2.3.1. $[Mn(dca)_2(H_2O)_2]_n \cdot (hmt)_n$ (**1**)

A methanolic solution (10 ml) of hmt (1 mmol, 0.140 g) was added dropwise to an aqueous solution (5 ml) of manganese (II) chloride tetrahydrate (1 mmol, 0.197 g) with stirring. To this reaction mixture an aqueous solution (5 ml) of sodium dicyanamide (2 mmol, 0.178 g) was poured slowly. After stirring for 30 min, the clear solution was filtered and the filtrate was kept in a $CaCl_2$ desiccator. After a few days, colorless single crystals suitable for X-ray analysis were obtained. Yield: 75%. *Anal.* Calc. for $C_{10}H_{16}MnN_{10}O_2$: C, 33.03; H, 4.40; N, 38.53. Found: C, 33.02; H, 4.42; N, 38.52%. IR spectra: 3490–3190(s,v,br), 3094(vw), 294(s), 2932(w), 2886(w), 2292(vs), 2244(vs), 2176(vs), 1669(w), 1460(s), 1370(s), 1336(vs), 1237(vs), 1237(vs), 1006(vs), 937(vw), 807(w), 696(s), 677(w), 532(w), 511(w) cm^{-1}.

2.3.2. $[Co(dca)_2(H_2O)_2]_n \cdot (hmt)_n$ (**2**)

A methanolic solution (10 ml) of cobalt nitrate hexahydrate (1 mmol, 0.291 g) was added dropwise with constant stirring to a mixture of hmt (1 mmol, 0.140 g) dissolved in methanol (5 ml) and sodium dicyanamide (2 mmol, 0.178 g) dissolved in water (5 ml). A pink colored species separated out from the reaction mixture. The single crystals suitable for X-ray analysis were obtained by diffusing the methanolic solution (10 ml) of cobalt nitrate hexahydrate on aqueous solution (10 ml) of hmt and sodium dicyanamide (1:2) in a corked tube. The pink colored single crystals were found at the junction of the two solutions after a few days. Yield: 78%. *Anal.* Calc. for $C_{10}H_{16}CoN_{10}O_2$: C, 32.67; H, 4.36; N, 38.12. Found: C, 32.65; H, 4.32; N,