Polyhedron 74 (2014) 57–66

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Discrete systems and two-dimensional coordination polymers containing potentially multidentate and bridging inorganic anions: Observation of a new type of two-dimensional topology

Arpita Biswas [a], Arpita Jana [a], Sohini Sarkar [a], Hazel A. Sparkes [b,c], Judith A.K. Howard [b], Núria Aliaga-Alcalde [d,*], Sasankasekhar Mohanta [a,*]

[a] Department of Chemistry, University of Calcutta, 92 A.P.C. Road, Kolkata 700 009, India
[b] Department of Chemistry, University of Durham, University Science Laboratories, South Road, Durham DH1 3LE, United Kingdom
[c] ISIS Facility, Rutherford Appleton Laboratory, Harwell Oxford, Didcot, Oxfordshire OX11 0QX, United Kingdom
[d] ICREA – Institut de Ciència de Materials de Barcelona (ICMAB-CSIC), Campus de la UAB, 08193 Bellaterra, Spain

ARTICLE INFO

Article history:
Received 9 December 2013
Accepted 24 February 2014
Available online 4 March 2014

Keywords:
Coordination polymer
Bridging ligand
Cyanometalates
Magnetic properties
Diamine
Two-dimensional

ABSTRACT

The work in this report deals with seven compounds of composition $\{[Cu^{II}(dmpn)_2]_3[Fe^{III}(CN)_6]_2{\cdot}6H_2O\}_n$ (**1**), $\{[Cu^{II}(dmpn)_2]_3[Co^{III}(CN)_6]_2{\cdot}6H_2O\}_n$ (**2**), $\{[Cu^{II}(dmpn)_2]_3[Cr^{III}(CN)_6]_2{\cdot}4H_2O\}_n$ (**3**), $\{[Cu^{II}(dmpn)][Ni^{II}(CN)_4]{\cdot}H_2O\}_n$ (**4**), $[\{Cu^{II}(dmpn)_2Cl\}\{Cu^{II}(dmpn)_2(H_2O)\}][Ag^{I}(CN)_2]Cl_2$ (**5**), $[(Cu^{II}(dmpn)_2(dicyanamide)_2]$ (**6**) and $[(Ni^{II}(dmpn)_2(dicyanamide)_2]$ (**7**), where dmpn = 2,2-dimethyl-1,3-diaminopropane. Syntheses, characterization and crystal structures of **1**–**7** along with variable-temperature (2–300 K) magnetic properties of **1** and **3** are described. Compounds **1**–**4** are cyanide-bridged two-dimensional coordination polymers. Twelve metal-membered ring is formed in **1**–**3**, while both four and eight metal-membered rings are formed in **4**. On the other hand, dicyanoargentate(I) in **5** is noncoordinated and dicyanamide in **6** and **7** behaves as monodentate terminal ligand. The coordination polymers in **1**–**4** and the discrete systems in **5**–**7** are self-assembled by hydrogen bonding interactions to generate overall three-dimensional supramolecular topologies. A novel structural aspect, two-dimensional network containing both four and eight metal-membered rings, has been observed in the copper(II)–tetracyanonickelate(II) compound **4**. Magnetic studies reveal ferromagnetic interaction between Cu^{II} and Cr^{III} in **3**. In addition, spin–orbit coupling of low-spin Fe^{III} or weak antiferromagnetic interaction along with intermolecular antiferromagnetic interactions which exist between Cu^{II} and Fe^{III} are present in **1**.

1. Introduction

Inorganic ions such as azide (N_3^-), dicyanamide ($[N(CN)_2]^-$), dicyanoargentate(I) ($[Ag(CN)_2]^-$), tetracyanonickelate(II) ($[Ni(CN)_4]^{2-}$), hexacyanometalate(III) ($[M(CN)_6]^{3-}$, M = Fe, Cr, Co, Mn) and hexacyanoferrate(II) ($[Fe(CN)_6]^{4-}$) have been widely utilized in coordination chemistry. In some systems, they behave as noncoordinating anions [1–11], while in some other systems, they behave as monodentate terminal ligands [12–15]. There is also the potential for them to act as bridging ligands in various ways. For example: possible bridging modes of azide are $\mu_{1,1}$- [16–18], $\mu_{1,3}$- [16,19], $\mu_{1,1,1}$- [20], $\mu_{1,1,3}$- [21,22], $\mu_{1,1,1,1}$- [23], and $\mu_{1,1,3,3}$- [24]; possible bridging modes of dicyanamide are $\mu_{1,5}$- [3,25,26], $\mu_{1,3}$- [3,27], $\mu_{1,1,5}$- [3,28], $\mu_{1,3,5}$- [3,29], $\mu_{1,1,3,5}$- [3,30] and $\mu_{1,1,3,5,5}$- [3,31]; only possible bridging mode of $[Ag(CN)_2]^-$ involves both the cyanide groups [7,8,13,32]. $[Ni(CN)_4]^{2-}$ can coordinate with metal ions through two [33–36], three [37,38] or all the four [32,39–42] cyanide groups; $[M(CN)_6]^{3-/4-}$ has been found to coordinate with metal ions through two [43–50], three [43,51–56], four [43,57–60] or six [43,61–66] cyanide moieties. With these anionic/terminal/bridging moieties, several discrete or polymeric coordination compounds have been reported. Some of such systems occupied a dominating position in molecular magnetism as well [5,16–19,22,43,49,52,55,59,60]. It is also known that the noncoordinating nitrogen atoms of the above mentioned bridging ligands can act as hydrogen bond acceptor to generate self-assemblies [4–10].

We have noted that there is no reported example containing 2,2-dimethyl-1,3-diaminopropane (dmpn) as the blocking ligand and dicyanamide/dicyanoargentate(I)/tetracyanonickelate(II)/hexacyanoferrate(III)/hexacyanocobaltate(III)/hexacyanochromate(III) as inorganic anion/ligand and the main focus of this investigation is to explore this aspect with the expectation to get new coordination

* Corresponding authors. Tel.: +91 9433883751 (S. Mohanta).
E-mail addresses: nuria.aliaga@icrea.cat (N. Aliaga-Alcalde), sm_cu_chem@yahoo.co.in (S. Mohanta).

http://dx.doi.org/10.1016/j.poly.2014.02.037
0277-5387/

network. Accordingly, we have attempted to isolate copper(II)/nickel(II) systems containing 2,2-dimethyl-1,3-diaminopropane (will be abbreviated hereafter as dmpn) and dicyanamide/dicyanoargentate(I)/tetracyanonickelate(II)/hexacyanoferrate(III)/hexacyanocobaltate(III)/hexacyanochromate(III), and have been able to isolate six copper(II) and one nickel(II) complex. The compositions of the isolated seven compounds are $\{[Cu^{II}(dmpn)_2]_3[Fe^{III}(CN)_6]_2{\cdot}6H_2O\}_n$ (**1**), $\{[Cu^{II}(dmpn)_2]_3[Co^{III}(CN)_6]_2{\cdot}6H_2O\}_n$ (**2**), $\{[Cu^{II}(dmpn)_2]_3[Cr^{III}(CN)_6]_2{\cdot}4H_2O\}_n$ (**3**), $\{[Cu^{II}(dmpn)][Ni^{II}(CN)_4]{\cdot}H_2O\}_n$ (**4**), $[\{Cu^{II}(dmpn)_2Cl\}\{Cu^{II}(dmpn)_2(H_2O)\}][Ag^{I}(CN)_2]Cl_2$ (**5**), $[(Cu^{II}(dmpn)_2(dicyanamide)_2]$ (**6**) and $[(Ni^{II}(dmpn)_2(dicyanamide)_2]$ (**7**). Herein, we report the syntheses, characterization and molecular and supramolecular structures of **1–7** along with variable-temperature (2–300 K) magnetic properties of **1** and **3**.

2. Experimental

2.1. Materials and physical methods

All the reagents and solvents were purchased from commercial sources and used as received. Elemental (C, H and N) analyses were performed on a Perkin-Elmer 2400 II analyzer. IR spectra were recorded, from KBr disks, in the region 400–4000 cm^{-1} on a Bruker-Optics Alpha-T spectrophotometer. Magnetic measurements were carried out in the "Unitat de Mesures Magnètiques (Universitat de Barcelona)" on polycrystalline samples with a Quantum Design SQUID MPMS-XL magnetometer working in the 2–300 K range. The magnetic fields used were 0.03 (from 2 to 30 K) and 1.0 T (from 2 to 300 K) for **1** and 0.03 (from 2 to 30 K) and 0.5 T (from 2 to 300 K) for **3**, respectively.

2.2. Synthesis

2.2.1. $\{[Cu^{II}(dmpn)_2]_3[Fe^{III}(CN)_6]_2{\cdot}6H_2O\}_n$ (1), $\{[Cu^{II}(dmpn)_2]_3[Co^{III}(CN)_6]_2{\cdot}6H_2O\}_n$ (2) and $\{[Cu^{II}(dmpn)_2]_3[Cr^{III}(CN)_6]_2{\cdot}4H_2O\}_n$ (3)

An aqueous solution (10 mL) of $K_3[Fe^{III}(CN)_6]$ (for **1**; 0.033 g, 0.1 mmol)/$K_3[Co^{III}(CN)_6]$ (for **2**; 0.032 g, 0.1 mmol)/$K_3[Cr^{III}(CN)_6]$ (for **3**; 0.033 g, 0.1 mmol) was added dropwise to a blue aqueous solution (50 mL) containing copper(II) chloride (0.020 g, 0.15 mmol) and dmpn (0.031 g, 0.3 mmol). The color of the mixture changed to green for **1** but remained almost unchanged for **2** and **3**. Small amounts of a green (for **1**) or blue (for **2** and **3**) precipitate appeared after a few minutes, which was filtered off and the filtrate was kept undisturbed. After a few days, a crystalline compound (green for **1**; blue for **2** and **3**) containing diffraction quality single crystals deposited, which was collected by filtration, washed with cold water and air dried.

Data for **1**: Yield: 0.055 g (82%). *Anal.* Calc. for $C_{42}H_{96}N_{24}O_6Cu_3Fe_2$ (1335.72): C, 37.77; H, 7.24; N, 25.17. Found: C, 38.02; H, 7.08; N, 25.36%. FTIR (KBr, cm^{-1}): 3447m [$\nu_{as}(H_2O)$], 2116s and 2085w [ν(CN)].

Data for **2**: Yield: 0.046 g (68%). *Anal.* Calc. for $C_{42}H_{96}N_{24}O_6Cu_3Co_2$ (1341.89): C, 37.59; H, 7.21; N, 25.05. Found: C, 37.32; H, 7.36; N, 24.87%. FTIR (KBr, cm^{-1}): 3444m [$\nu_{as}(H_2O)$], 2129s, [ν(CN)].

Data for **3**: Yield: 0.030 g (46%). *Anal.* Calc. for $C_{42}H_{92}N_{24}O_4Cu_3Cr_2$ (1291.99): C, 39.05; H, 7.18; N, 26.02. Found: C, 39.18; H, 7.35; N, 26.24%. FTIR (KBr, cm^{-1}): 3439m [$\nu_{as}(H_2O)$], 2128m and 2105sh [ν(CN)].

2.2.2. $\{[Cu^{II}(dmpn)][Ni^{II}(CN)_4]{\cdot}H_2O\}_n$ (4), $[\{Cu^{II}(dmpn)_2Cl\}\{Cu^{II}(dmpn)_2(H_2O)\}][Ag^{I}(CN)_2]Cl_2$ (5), $[(Cu^{II}(dmpn)_2(dicyanamide)_2]$ (6) and $[(Ni^{II}(dmpn)_2(dicyanamide)_2]$ (7)

An aqueous solution (10 mL) of $K_2[Ni(CN)_4]$ (for **4**; 0.060 g, 0.25 mmol)/$K[Ag(CN)_2]$ (for **5**; 0.051 g, 0.5 mmol)/sodium dicyanamide (for **6** and **7**; 0.032 g, 0.5 mmol) was added dropwise to a blue aqueous solution (25 mL) containing copper(II) chloride (for **4–6**; 0.034 g, 0.25 mmol)/nickel(II) chloride hexahydrate (for **7**; 0.059 g, 0.25 mmol) and dmpn (0.051 g, 0.5 mmol). The color of the solution remained almost unchanged for **4** and **6** but changed to blue-violet for **5** and **7**. The solution was filtered to remove any suspended particles and the clear filtrate was kept undisturbed. After a few days, crystalline compound containing

Table 1
Crystallographic data for **1–7**.

	1	2	3	4	5	6	7
Formula	$C_{42}H_{96}N_{24}O_6Cu_3Fe_2$	$C_{42}H_{96}N_{24}O_6Cu_3Co_2$	$C_{42}H_{92}N_{24}O_4Cu_3Cr_2$	$C_9H_{16}N_6OCuNi$	$C_{22}H_{56}N_{10}OCl_3Cu_2Ag$	$C_{14}H_{28}N_{10}Cu$	$C_{14}H_{28}$ $N_{10}Ni$
FW	1335.75	1341.91	1292.02	346.53	818.07	400.00	395.17
Crystal color	green	blue	blue	blue	blue-violet	blue	blue-violet
Crystal system	triclinic	triclinic	monoclinic	monoclinic	tetragonal	trigonal	trigonal
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P2_1/c$	$P4_32_12$	$R\bar{3}$	$R\bar{3}$
a (Å)	8.99310(10)	8.96900(10)	11.4542(2)	11.2301(2)	12.3376(2)	25.0731(6)	24.6813(4)
b (Å)	13.0296(2)	13.0191(2)	16.7952(3)	9.7276(2)	12.3376(2)	25.0731(6)	24.6813(4)
c (Å)	15.9704(3)	15.9201(3)	16.3056(3)	13.5585(3)	47.2529(13	8.2346(2)	8.39530(10)
α (°)	110.3000(10)	110.5550(10)	90	90.00	90.00	90.00	90.00
β (°)	99.9290(10)	99.7140(10)	101.8410(10)	104.7220(10)	90.00	90.00	90.00
γ (°)	99.2320(10)	99.4040(10)	90	90.00	90.00	120(2)	120.00
V (Å^3)	1678.98(4)	1664.99(4)	3070.05(10)	1432.53(5)	7192.7(3)	4483.21(19)	4428.97(11)
Z	1	1	2	4	8	9	9
T (K)	120(2)	120(2)	120(2)	120(2)	120(2)	120(2)	120(2)
2θ	2.80–54.20	2.82–54.20	3.52–56.56	5.22–50.04	3.42–56.56	5.30–52.74	6.60–61.62
μ(Mo Kα) (mm^{-1})	1.413	1.488	1.423	2.796	1.965	1.115	1.005
ρ_{calc} (g cm^{-3})	1.321	1.338	1.398	1.607	1.511	1.333	1.333
F(000)	703	705	1358	708	3376	1899	1890
Absorption-correction	semi-empirical from equivalents	semi-empirical from equivalents	semi-empirical from equivalents	semi-empirical from equivalents	semi-empirical from equivalents	analytucal	semi-empirical from equivalents
Index ranges	$-11 \leqslant h \leqslant 11$ $-16 \leqslant k \leqslant 16$ $-20 \leqslant l \leqslant 20$	$-11 \leqslant h \leqslant 11$ $-16 \leqslant k \leqslant 16$ $-20 \leqslant l \leqslant 20$	$-15 \leqslant h \leqslant 15$ $-22 \leqslant k \leqslant 22$ $-21 \leqslant l \leqslant 21$	$-13 \leqslant h \leqslant 13$ $-9 \leqslant k \leqslant 11$ $-16 \leqslant l \leqslant 16$	$-15 \leqslant h \leqslant 15$ $-15 \leqslant k \leqslant 15$ $-62 \leqslant l \leqslant 62$	$-35 \leqslant h \leqslant 35$ $-34 \leqslant k \leqslant 35$ $-11 \leqslant l \leqslant 11$	$-34 \leqslant h \leqslant 35$ $-35 \leqslant k \leqslant 33$ $-12 \leqslant l \leqslant 11$
Reflections collected	21391	21186	41997	8470	80307	28169	26235
Independent reflections (R_{int})	7423/0.0423	7362/0.0361	7613/0.0264	2535/0.0265	8667/0.0455	3027/0.0299	2978/0.0298
R_1[a]/wR_2[b] [$I > 2\sigma(I)$]	0.0391/0.0908	0.0351/0.0814	0.0238/0.0613	0.0272/0.0681	0.0310/0.0731	0.0237/0.0620	0.0230/0.0551
R_1[a]/wR_2[b] [for all F_o^2]	0.0583/0.1014	0.0497/0.0895	0.0281/0.0638	0.0318/0.0712	0.0352/0.0749	0.0272/0.0638	0.0260/0.0564

[a] $R_1 = [\Sigma||F_o| - |F_c||/\Sigma|F_o|]$.
[b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$.