

Dimeric Ni(II)₂ and polymeric Ni(II)₄Fe(II) type complexes bridged with Cl[−] and CN[−] ligands: X-ray structures and magnetic properties of a dimeric complex of [(tren)Ni(μ-Cl)₂Ni(tren)](ClO₄)₂ and a polymeric complex of {[Fe(CN)₆][Ni(tren)]₂[Ni(tren)(H₂O)]₂}Cl₂(ClO₄)₂·4H₂O



Joo-Eun Jee, Chee-Hun Kwak *

Department of Chemistry, Suncheon National University, Suncheon, Jeonnam 540-742, Republic of Korea

ARTICLE INFO

Article history:

Received 11 February 2013

Accepted 8 April 2013

Available online 16 April 2013

Keywords:

Tren

Ferrocyanide

Ni(II)₂ dimer

Ferromagnetic coupling

Ni(II)₄Fe(II) coordination polymer

Spin crossover

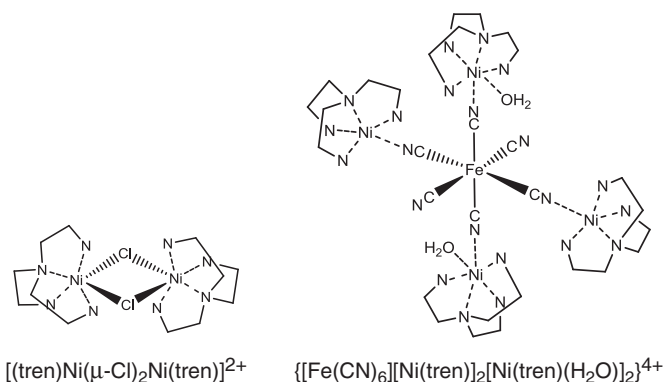
ABSTRACT

A dimeric complex of [(tren)Ni(μ-Cl)₂Ni(tren)](ClO₄)₂ (**1**) and a polymeric complex of {[Fe(CN)₆][Ni(tren)]₂[Ni(tren)(H₂O)]₂}Cl₂(ClO₄)₂·4H₂O (**2**), are isolated from the reaction of potassium ferricyanide, nickel chloride and tren and their X-ray structures and magnetic properties were characterized. Two [Ni(tren)]²⁺ units are linked through bis μ-Cl ligands forming dimeric structure of **1**. In complex **2**, there are two kinds of Ni(II) unit, terminal ([Ni(tren)(H₂O)]²⁺) and bridged ([Ni(tren)]²⁺), and this bridged [Ni(tren)]²⁺ units are linked with two different Fe(II) ions through μ-CN ligands forming one-dimensional polymeric rectangular chain. **1** shows a weak ferromagnetic coupling between two Ni(II) ions and **2** shows spin crossover in Fe(II) ion.

© 2013 Elsevier B.V. All rights reserved.

The coordination chemistry derived from tren, tris(2-aminoethyl)amine, and ligand is interesting because it implies a wide variety of biochemical and catalytic activities [1–5]. Also, this multidentate ligand has the great flexibility in coordination pattern and it can be applied in crystal engineering, such as preparation of multimetallic complexes, two or three dimensional structures, etc. [6–11]. Ferricyanide or ferrocyanide, [Fe(CN)₆]^{x−} (x = 3 or 4), has been revealed as a useful building block to produce cyanide bridged networks with a large variety of multi-dimensional structures. Combining with the [Fe(CN)₆]^{x−}, polyaza complexes produced one-dimensional chain, two-dimensional honeycomb-like structure, and three-dimensional cubane structures [12–20] and some of these systems are applied for the molecular magnetic materials [15–20]. A few cases have been reported from the combination of tren and ferricyanide or ferrocyanide, [(tren)Cu(NC)Fe(CN)₄(CN)Cu(tren)]·12H₂O, leads to a non-linear chain, [21], and heptanuclear [(Cu(tren)CN)₆Fe]⁸⁺ cation and pentanuclear [(Cu(tren)CN)₄Fe(CN)₂]⁴⁺ cation, form three-dimensional H-bonding networks [22], and [Ni(tren)]₃[Fe(CN)₆]₂·6H₂O has a three-dimensional structure [23]. Here, we obtained dimeric complex of [(tren)Ni(μ-Cl)₂Ni(tren)](ClO₄)₂ (**1**) and one-dimensional polymeric ring chain of {[Fe(CN)₆][Ni(tren)]₂[Ni(tren)(H₂O)]₂}Cl₂(ClO₄)₂·4H₂O (**2**), by the reaction of potassium ferricyanide, nickel chloride and tren. In this

paper, single crystal X-ray structures and magnetic properties of **1** and **2** are discussed.



Complexes **1** and **2** are obtained from the reaction of nickel(II) chloride, potassium ferricyanide and tren [24]. We obtained **2** as a Fe(II) complex although we used ferricyanide [13,22]. These complexes were characterized by elemental analysis and spectrochemical method inclusive single crystal X-ray structural analysis [25]. ORTEP view of a symmetry-generated unit for the cation of **1** is shown in Fig. 1. The cation of **1** has a centrosymmetry and two [Ni(tren)]²⁺

* Corresponding author. Tel.: +82 61 750 3636; fax: +82 61 750 3308.

E-mail address: chkwak@sunchon.ac.kr (C.-H. Kwak).

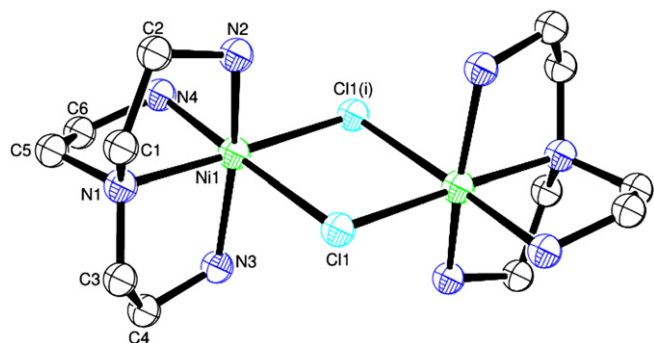


Fig. 1. ORTEP view of the atomic numbering scheme for non-hydrogen atoms of a symmetric unit of **1** with 50% probability thermal ellipsoids. Two perchlorate anions are omitted for the clarity. Symmetry code: (i); $1 - x, 2 - y, 1 - z$. Selected bond lengths (Å) and angles (degree): Ni1–N4 2.076(3), Ni1–N1 2.105(2), Ni1–N2 2.107(3), Ni1–N3 2.115(3), Ni1–Cl1 2.5618(9), Ni1–Cl1(i) 2.4453(8), Cl1–Ni1–Cl1(i) 85.32(3), Ni1–Cl1–Ni1(i) 94.68(3).

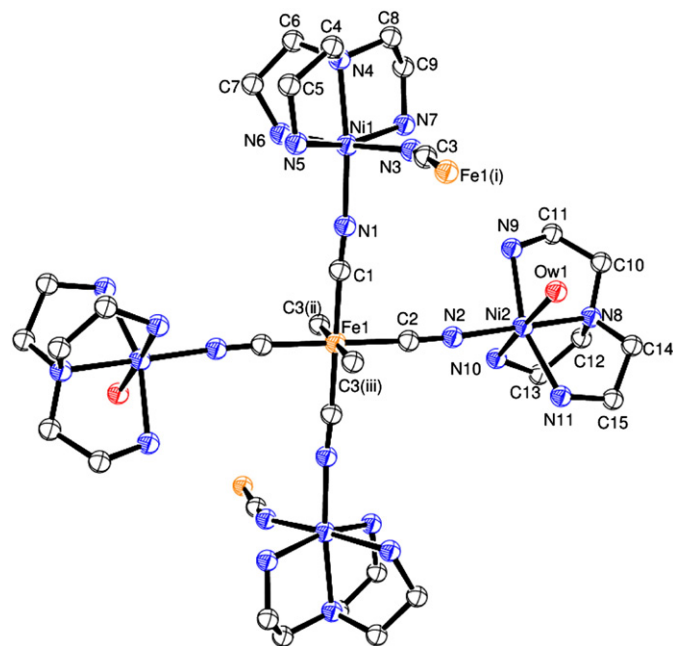


Fig. 2. ORTEP view of the atomic numbering scheme for non-hydrogen atoms of a symmetric unit of **2** with 50% probability thermal ellipsoids. Two perchlorates and two chlorides, and four packing water molecules are omitted for the clarity. Symmetry code: (i); $1 - x, 1 - y, 1 - z$, (ii); $-1 + x, y, z$, (iii); $-x, 1 - y, 1 - z$. Selected bond lengths (Å) and angles (degree): Ni1–N1 2.058(7), Ni1–N3 2.155(7), Ni1–N4 2.138(6), Ni1–N5 2.110(7), Ni1–N6 2.123(7), Ni1–N7 2.111(7), Ni2–N2 2.030(7), Ni2–N8 2.117(7), Ni2–N10 2.082(7), Ni2–N9 2.134(7), Ni2–N11 2.119(8), Ni2–OW1 2.184(7), Fe1–C1, 1.911(8) Fe1–C2, 1.913(8), Fe1–C3(i) 1.914(8), N1–Ni1–N5 99.4(3), N1–Ni1–N7 97.2(3), N5–Ni1–N7 161.8(3), N2–Ni2–N8 174.6(3), N2–Ni2–N9 96.8(3), N2–Ni2–N10 91.3(3), C3–Fe1–C2(ii) 89.3(3), C3(ii)–Fe1–C2 90.7(3), C1–Fe1–C2 88.8(3), C1–Fe1–C2(iii) 91.2(3), C2–Fe1–C2(iii) 180.000(2).

units are linked through μ -Cl ligands, forming dimeric structure. The geometry around each Ni(II) ion is a distorted octahedron with two μ -chloro ligands at *cis*-position. Average bond distance between Ni(II) ions and four nitrogens of tren is 2.101(3) Å and bond distance between Ni(II) ions and tertiary nitrogen of N3 (2.115(3) Å) is slightly longer than those between Ni(II) ions and primary nitrogens. Bond distances between Ni1–Cl1 and Ni1–Cl1($1 - x, 2 - y, 1 - z$) are 2.562(1) and 2.445(1) Å, respectively. Bond angles of Cl1($1 - x, 2 - y, 1 - z$)–Ni1–Cl1 and Ni1($1 - x, 2 - y, 1 - z$)–Cl1–Ni1 are 85.2(3)° and 94.7(3)°, respectively. Dihedral angles of N2–Ni1–N3 and N4–Ni1–Cl1 are 161.9(1)° and 177.4(1)°, respectively.

ORTEP view of a symmetric unit of **2** without anions and packing waters is shown in Fig. 2. The geometries of four Ni(II) ions and Fe(II) ion adopted a distorted octahedron. There are two kinds of Ni(II) ions with different coordination modes: one (Ni2) coordinates four nitrogens of tren, and a nitrogen of μ -NC ligand and a water ligand (terminal Ni, [(μ -CN)Ni²⁺(tren)(H₂O)]), another (Ni1) coordinates four nitrogens of tren and two nitrogens of μ -CN ligands of two different ferrocyanide units with a *cis* arrangement (bridged Ni, [(μ -CN)₂Ni²⁺(tren)]). This coordination mode of Ni(II) ion forms a polymeric rectangular chain prolonged along the *a*-axis. Resulting polymeric structure is shown in Fig. 3. Average Ni(II)–N distances between tren and bridged Ni(II) ion (Ni1) and that between tren and terminal Ni(II) ion (Ni2) are similar: for Ni(1) and Ni(2) are 2.120(7) and 2.113(8) Å, respectively, and Ni1–N(μ -NC) distances (Ni1–N1; 2.058(7), Ni1–N3 2.155(7) Å) are somewhat longer than Ni2–N(μ -NC) distance (Ni2–N2; 2.030(7) Å). Fe–C distances in Fe–CN–Ni (bridged) are 1.911(8) Å for Fe1–C1 and 1.914(8) Å for Fe1–C3($1 + x, y, z$), which are similar to the Fe–C distance in Fe–CN–Ni (terminal) of 1.913(8) Å (Fe1–C2). Ni2–OW1 (water ligand) distance is 2.184(7) Å. The bond angle arranged by two nitrogens of μ -NC ligands and bridged Ni(II) ion (N1–Ni1–N3) is 95.2(3)°. The bond angles arranged by two carbons of μ -CN ligands linked with bridged Ni(II) ion and Fe(II) ion are 92.5(3)° for C3–Fe1–C1($-1 + x, y, z$) and 87.5(3)° for C3–Fe1–C1($1 - x, 1 - y, 1 - z$), and those arranged by two carbons of μ -CN ligands linked with terminal Ni(II) ion and Fe(II) ion are 89.3(3)° for C3–Fe1–C2($1 - x, 1 - y, 1 - z$) 90.7(3)° and for C3($1 - x, 1 - y, 1 - z$)–Fe1–C2. The bond angles arranged by a carbon of μ -CN ligand linked with a terminal Ni(II) ion and a carbon of μ -CN ligand linked with bridged Ni(II) ion, and Fe(III) ion are 88.8(3)° for C1–Fe1–C2 and 91.2(3)° for C1–Fe1–C2($-x, 1 - y, 1 - z$).

The magnetic susceptibilities, χ , of **1** and **2** are measured on powdered sample in an applied field of 1000 Oe between 2 and 300 K, and are plotted as $\chi_M^{-1}(T)$ and $\mu_{\text{eff}}(T)$ ($\mu_{\text{eff}}(T) = [8\chi T]^{1/2}$) as shown

in Figs. 4 and 5, respectively. Effective magnetic moment of **1** is 3.75 μ_B at 300 K and it is gradually increased with decreasing temperature until 6 K (4.50 μ_B). Below 6 K, $\mu_{\text{eff}}(T)$ decreases to 4.35 μ_B at 2 K. The value of 3.75 μ_B at 300 K is a little smaller than the 4.0 μ_B expected for independent two spins of $g = 2, S = 1$, and is attributed to a low effective Landé g value of Ni(II). Above 2 K, $\chi^{-1}(T)$ can fit to the Curie–Weiss expression $\chi_M = C / (T - \theta)$ with $\theta = 5.07$ K ($C = 1.725$ emu K/mol) [26]. The magnetic properties show a weak ferromagnetic coupling between the two Ni(II) ions. Also, the magnetic susceptibility can be interpreted by using Heisenberg Dirac Van Vleck equation for spin coupled dimer with $S_A = S_B = 1$ as shown in Eq. (1) [27], where $x = J / kT$.

$$\chi_M = \frac{Ng^2\beta^2}{kT} \frac{2e^{2x} + 10e^{6x}}{1 + 3e^{2x} + 5e^{6x}} \quad (1)$$

The best fitting of the least-square analysis of magnetic data with the Eq. (1) leads to $J = 8.75 \pm 1.48$ cm⁻¹, $g = 1.802 \pm 0.003$ (see Supplementary materials). These obtained J and g values support the ferromagnetic coupling between two Ni(II) ions and the smaller value of 3.75 μ_B at 300 K. The effective magnetic moment of **2** is 8.67 μ_B at 300 K and it is gradually decreased until around 20 K with the value of 6.34 μ_B and below 20 K, it is dramatically decreased to 5.12 μ_B at 2 K. The value of 8.67 μ_B at 300 K is somewhat larger than the expected value (7.64 μ_B) of four independent spins of $g = 2, S = 1$ (Ni(II)) with a spin of $g = 2, S = 2$ (Fe(II) with a high spin) and the values of 6.34 μ_B at 20 K and 5.12 μ_B at 2 K are ranged closely to the expected value (5.66 μ_B) of four independent spins of $g = 2, S = 1$ (four Ni(II)s) with a spin of $g = 2, S = 0$ (Fe(II) with a low spin). Thus, this result, a dramatic change of magnetic moment

Download English Version:

<https://daneshyari.com/en/article/7749774>

Download Persian Version:

<https://daneshyari.com/article/7749774>

[Daneshyari.com](https://daneshyari.com)