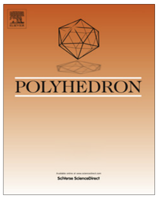
Polyhedron 56 (2013) 1–8

Contents lists available at SciVerse ScienceDirect

Polyhedron

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



Nickel(II) complexes with bridged polyamines

Kristína Matelková [a], Ján Moncol [a], Radovan Herchel [b], Ľubor Dlháň [a], Radoslava Ivaniková [a], Ingrid Svoboda [c], Zdĕnka Padĕlková [d], Anna Mašlejová [a,*]

[a] Department of Inorganic Chemistry, Slovak University of Technology in Bratislava, SK-812 37 Bratislava, Slovakia
[b] Department of Inorganic Chemistry, Faculty of Science, Palacky University, 17. Listopadu 12, CZ-771 46 Olomouc, Czech Republic
[c] Material Science, Darmstadt University of Technology, D-64287 Darmstadt, Germany
[d] Department of General and Inorganic Chemistry, Faculty of Chemical Technology, University of Pardubice, CZ-532 10 Pardubice, Czech Republic

ARTICLE INFO

Article history:
Received 13 February 2013
Accepted 13 March 2013
Available online 21 March 2013

Keywords:
Ni(II) complexes
Crystal structures
Magnetism
Bridging tetradentate amines

ABSTRACT

Three nickel(II) complexes $[Ni_2(\mu\text{-}trien)(trien)_2](ClO_4)_4$ (**1**), $\{[Ni_2(\mu\text{-}tren)_2(tren)](ClO_4)_4\cdot3{,}25H_2O\}_n$ (**2**) and $[Ni_3(\mu\text{-}tren)_2(tren)_2(H_2O)_2]Cl_6\cdot2H_2O$ (**3**) (*trien* = *N*,*N*′-bis(2-aminoethyl)ethane-1,2-diamine, *tren* = *N*,*N*′-bis(2-aminoethyl)-1,2-ethanediamine) were synthesized and structurally characterized. Complex **1** consists of dimeric $[Ni_2(\mu\text{-}trien)(trien)_2]^{4+}$ cation and perchlorate anions, compound **2** contains polymer chain of cation $\{[Ni_2(\mu\text{-}tren)_2(tren)]^{4+}\}_n$, perchlorate anions and uncoordinated water molecules, and structure of **3** consists of $[Ni_3((\mu\text{-}tren)_2(tren)_2(H_2O)_2]^{6+}$ cation, chloride anions and uncoordinated water molecules. All compounds exhibit octahedrally coordinated nickel atoms. Two nickel(II) atoms of $[Ni_2(\mu\text{-}trien)(trien)_2]^{4+}$ cation in **1** are bridged through one *trien* ligand, which is bidentate to both nickel(II) atoms. The central Ni(II) atom in complex **3** is associated with peripheral atoms with one arm of *tren* ligand bonded in tridentate fashion, similarly as two nickel(II) atoms in polymer of complex **2**. The magnetic behaviour of **1** and **2** complexes have been investigated in terms of magnetic susceptibility and magnetization. The magnetic analyses confirmed weak antiferromagnetic exchange between paramagnetic Ni(II) centres. The experimental observations were further confirmed and studied by DFT method at B3LYP/def2-TZVP level of theory for all compounds.

1. Introduction

The aliphatic tetradentate amines like tripodal amine *N*,*N*′-bis(2-aminoethyl)-1,2-ethanediamine) (*tren*), and linear amine *N*,*N*′-bis(2-aminoethyl)ethane-1,2-diamine (*trien*) are often utilized in transition metal coordination chemistry. Usually, the above mentioned ligands act as terminal ligands and two left *cis* positions in octahedrally coordinated complexes can be used to formation of mononuclear and polynuclear compounds [1–12] or bimetallic networks by employing cyanidometallic or thiocyanatometallic complex anions [13–21].

Recently, we studied such bimetallic complexes containing *trien* as a blocking ligand and *diamagnetic* bridging cyanidometallic anions, in which weak antiferromagnetic exchange ($[Ni(trien)(cis\text{-}\mu^2\text{-}Ni(CN)_4)]$ and $[\{Ni(trien)\}_3(\mu^6\text{-}Co(CN)_6)](ClO_4)_3$) or very weak ferromagnetic exchange in ($[Ni(trien)(\mu^1\text{-}Ag(CN)_2)_2]$) was found [20]. However, using *paramagnetic* bridging cyanidometallic anions, such as $[Fe(CN)_6]^{3-}$ may result in formation of molecule-based magnets [22], e.g. $\{[Ni(tren)_2]_3[Fe(CN)_6]_2\cdot6H_2O\}_n$ e.g. (ferrimagnet with $T_c = 8$ K) [23] and similar systems were summarized in the detailed study of the metamagnetic behaviour of $\{[Ni(en)_2]_3[Fe(CN)_6]_2\cdot xH_2O\}_n$ (en = ethylenediamine and $x = 3, 2,$ or 0) coordination polymer acting as molecular magnetic sponge [24].

Furthermore, the *tren* and *trien* ligands can be also utilized as bridging ligands. In case of *tren* ligand, the trinuclear complex cations $[Ni_3(\mu\text{-}tren)_2(tren)_2(H_2O)_2]^{4+}$ [25] and one-dimensional polymers $\{[Ni_2(\mu\text{-}tren)_2(tren)]^{4+}\}_n$ [25,26] were reported. Surprisingly, only binuclear complexes containing $[Ni_2(\mu\text{-}trien)(trien)_2]^{4+}$ are reported [27–32].

The present paper describes the preparation, the structural and spectroscopic characterization of $[Ni_2(\mu\text{-}trien)(trien)_2](ClO_4)_4$ (**1**), $\{[Ni_2(\mu\text{-}tren)_2(tren)](ClO_4)_4\cdot3{,}25H_2O\}_n$ (**2**) and $[Ni_3(\mu\text{-}tren)_2(tren)_2(H_2O)_2]Cl_6\cdot2H_2O$ (**3**) and also the detail study of magnetic properties for **1** and **2** as representatives of *trien* and *tren* ligands bridging modes. This study enriches our preliminary results presented on the conferences [33,34]. Furthermore, the origin and nature of magnetic exchange within reported complexes **1**–**3** is supported by theoretical investigation based on DFT utilizing B3LYP hybrid functional.

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* Corresponding author. Tel.: +421 2593 25 187; fax: +421 2524 93 198.
E-mail address: anna.maslejova@stuba.sk (A. Mašlejová).

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http://dx.doi.org/10.1016/j.poly.2013.03.028

2. Experimental

2.1. Synthesis

All reagents and solvents were purchased from commercial sources and used as received.

The first complex was prepared by chance to synthesize heterobimetallic cyanidometallate by slow diffusion of two aqueous solutions. One is a mixture of stoichiometric amounts of $Ni(ClO_4)_2\cdot 6H_2O$ and the ligand trien. The blue-violet solution was put into one side of an H-shaped vessel. The other side of the vessel contained an aqueous solution of $K_3[Fe(CN)_6]$. Within several days small blue-violet crystals of **1** suitable for single crystal X-ray crystallographic studies had formed.

Aqueous solution of $Ni(ClO_4)_2\cdot 6H_2O$ was mixed with aqueous solution of tren ligand. The violet crystals of compound **2** were formed by standing the reaction system.

The complex **3** was prepared from methanolic solution of $NiCl_2\cdot 6H_2O$ by drop wise addition of *tren* ligand under the stirring at room temperature, until the colour of solution become violet. The acetonitrile (ca 1 cm^3) and diethylether were then added. Resulting violet solid was dissolved in methanol and after a few weeks small violet crystals suitable for X-ray crystallographic studies were obtained.

Solutions used:

1. 0.025 g $K_3[Fe(CN)_6]$ (0.076 mmol) in 5 cm^3 water, 0.167 g $Ni(ClO_4)_2\cdot 6H_2O$ (0.046 mmol) and 0.067 g (0.046 mmol) *trien* in 5 cm^3 water.
2. 0.5 g $Ni(ClO_4)_2\cdot 6H_2O$ (1.67 mmol) in 10 cm^3 water, 0.3 g (2.05 mmol) *tren* in 10 cm^3 water.
3. 0.4 g $NiCl_2\cdot 6H_2O$ (1.68 mmol) in 5 cm^3 methanol, 0.3 g (2.05 mmol) *tren*.

Compound **1**: *Anal.* Calc. for $C_{18}H_{54}Cl_4N_{12}Ni_2O_{16}$: C, 48.04; H, 1.34; N, 12.45. Found: C, 48.18; H, 1.45; N, 11.96%.

Compound **2**: *Anal.* Calc. for $C_{18}H_{60.5}Cl_4N_{12}Ni_2O_{19.25}$: C, 49.10; H, 1.23; N, 11.36. Found: C, 48.81; H, 1.45; N, 11.96%.

Compound **3**: *Anal.* Calc. for $C_{24}H_{80}Cl_6N_{16}Ni_3O_4$: C, 27.56; H, 7.71; N, 21.43. Found: C, 27.34; H, 7.09; N, 21.45%. Despite satisfactory results of elemental analysis, FTIR and X-ray analysis, the bulk material was probably contaminated by unknown impurity which prevented us to properly analyse its properties.

2.2. Physical measurements

Elemental analysis (C, H, N) was carried out on Flash EA 1112 (ThermoFinnigan). IR spectra were measured on Magna-FTIR-750 spectrometer (Nicolet) in KBr pellets in the 4000–400 cm^{-1} region.

Temperature dependence of the magnetization at $B = 0.1$ T from 2 to 300 K and the isothermal magnetizations at $T = 2.0$ and 4.6 K up to $B = 7$ T were measured using a SQUID magnetometer (MPMS XL-7, Quantum Design). The mean susceptibility was calculated as $\chi_{mol} = \mu_0 M_{\mathrm{mol}}/B$ and corrected for the underlying diamagnetism of the constituent atoms using Pascal constants [35]. The effective magnetic moment has been calculated as usual: $\mu_{\mathrm{eff}}/\mu_{\mathrm{B}} = 798(\chi' T)^{1/2}$ when SI units are employed.

Single-crystal X-ray diffraction experiments for complexes **1** and **2** have been performed using Bruker-Nonius KappaCCD diffractometer at 150 K and for complex **3** using Xcalibur S CCD apparatus (Oxford Diffraction) at 293 K. The diffraction intensities were corrected for Lorentz and polarization factors. The empirical absorption corrections were performed by multi-scan method using SADABS (**1**, **2**) [36] or SCALE3 ABSPACK in CRYSALISPRO (**3**) [37]. The structures were solved by the direct methods with SHELXS-97 [38] or SIR-2011 [39], and refined by the full-matrix least squares procedure with SHELXL-97 [38]. Geometrical analyses were performed using SHELXL-97 and the structures were drawn using the XP in SHELXTL [38]. Final crystal data and structure refinement parameters are given in Table 1. Selected bond distances are given in Table 2.

The crystal structures of **1** and **2** show variable positional disorders of perchlorate anions (see Supplementary Figs. S1 and S2). The disordered perchlorate anions of **1** and **2** have been modelled using SADI [for O···O distances], DFIX or SADI [for Cl–O distances], and EADP commands. The crystal structure of **3** shows positional disordered ethylene groups (see Supplementary Fig. S3). The disordered ethylene groups of **3** have been modelled using SADI [for C···N and N···N distances]; SIMU and DELU commands.

3. Results and discussion

3.1. Crystal structures

The structure of **1** is built up of dimeric $[Ni_2(\mu\text{-}trien)(trien)_2]^{4+}$ cations and perchlorate anions (Fig. 1). Six nitrogen atoms of *trien* ligands surround each Ni(II) atom in octahedral arangement with an average Ni–N distance of 2.13 Å (Table 2). The chelating terminal *trien* ligand in **1** is coordinated in cis-α configuration [3] (Fig. 1). Two ligands *trien* are coordinated to each Ni(II) atom in tetradentate fashion, while the third one is making the bridge and coordinates in bidentate fashion to each the Ni(II) atom forming dimeric cation. The perchlorate anions are involved into the hydrogen bond network with the N–H and $N–H_2$ moieties of the *trien* ligands. The crystal structures of other complexes with the dimeric $[Ni_2(\mu\text{-}trien)(trien)_2]^{4+}$ cations and various inorganic [NO_3^-, Cl^-, $Ge_4S_{10}^{4-}$, $Ge_4Se_{10}^{4-}$] or organic [4,4′-biphenyldisulfonate] anions have been prepared and structural characterized [28–32]. The crystal structure of similar complex $[Ni_2(\mu\text{-}tren)(tren)_2](ClO_4)_4$ is also known [27].

The crystal structure of **1** consists of complex dimeric $[Ni_2(\mu\text{-}trien)(trien)_2]^{4+}$ cations and perchlorate anions connecting through N–H···O hydrogen bond (see Supplementary Table S1) between amine groups of *trien* ligands and perchlorate oxygen atoms into 2-D supramolecular networks (see Supplementary Fig. S5).

The crystal structure of **2** contains polymer chain of cation $\{[Ni_2(\mu\text{-}tren)_2(tren)]^{4+}\}_n$, perchlorate anions and water molecules. The structure of $\{[Ni_2(\mu\text{-}tren)_2(tren)]^{4+}\}_n$, shown in Fig. 2, consists of *zig-zag* chain, obtaining three crystallographically independent Ni(II) atoms. The Ni1 and Ni2 atoms lay in special positions of centres symmetry and both ones are octahedral coordinated by two *tren* molecules, which act as tridentate ligands, with each *tren* ligand having a pendant arm ending with primary amine. The Ni3 atom is hexacoordinated by a single *tren* ligand in tetradentate fashion, fifth and sixth positions are occupied by nitrogen atoms from one pendant primary amine from *tren* molecules bound tridentate to neighbouring Ni1 and Ni2 atoms. However, the free arm of *tren* from Ni1 atom (N4) is coordinated oposite tetriary nitrogen atom (N11) of *tren* molecule and on the other hand, the free arm from Ni2 (N1) opposite primary nitrogen atom (N8) from *tren* ligand. The distances between Ni1–N atoms are in the range 2.130(3)–2.160(3) Å (Table 2), between Ni2–N atoms 2.124(3)–2.157(3) Å and Ni3–N atoms 2.094(3)–2.195(2) Å (Table 2), respectively. Another pseudopolymorph [40] $\{[Ni_2(\mu\text{-}tren)_2(tren)](ClO_4)_4\cdot H_2O\}_n$ of compound **2** has been also published [25].

The chain of cation $\{[Ni_2(\mu\text{-}tren)_2(tren)]^{4+}\}_n$, perchlorate anions and water molecules are connected into 2-D supramolecular networks through N–H···O hydrogen bonds (see Supplementary Table S1) between amine groups of *tren* ligands and oxygen atoms of perchlorate anions or water molecules (see Supplementary