Inorganica Chimica Acta 416 (2014) 215–221

Contents lists available at ScienceDirect

Inorganica Chimica Acta

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

Synthesis and characterization of nickel(II) and copper(II) tricyanomethanide complexes with tris(2-aminoethyl)amine as co-ligand

Jun Luo, Yue Gao, Li-Juan Qiu, Bao-Shu Liu *, Xin-Rong Zhang *, Li-Li Cui, Feng Yang

School of Pharmacy, Second Military Medical University of PLA, Shanghai 200433, People's Republic of China

ARTICLE INFO

Article history:
Received 6 August 2013
Received in revised form 16 January 2014
Accepted 27 March 2014
Available online 5 April 2014

Keywords:
Tricyanomethanide
Tris(2-aminoethyl)amine
Nickel(II) complex
Copper(II) complex
Trinuclear structure
Magnetic property

ABSTRACT

Two new transition metal tricyanomethanide (tcm) complexes with tris(2-aminoethyl)amine (tren) as co-ligand, $[Ni(tren)(tcm)_2]$ (**1**) and $[Cu(tren)]_3{\cdot}(\mu_3\text{-tren}){\cdot}NO_3{\cdot}5tcm{\cdot}2H_2O$ (**2**), were synthesized and characterized by FT-IR spectrum, Thermogravimetry (TG) and single crystal X-ray diffraction analysis. In **1** each nickel(II) atom is coordinated to two tcm anions and one tren molecule to form a mononuclear complex with distorted octahedral geometry. In **2** three copper(II) atoms, each being chelated by a tetradentate tren ligand, are bridged by a μ_3-tren ligand to form a cationic trinuclear copper unit. Magnetic susceptibility measurement in the range 2–300 K indicates that there are weak ferromagnetic interactions in **1** (θ = 1.17 K, C = 1.17 $cm^3\ mol^{-1}\ K$, D = 3.5 cm^{-1}, g = 2.17, zJ' = 0.44 cm^{-1}) and **2** (θ = 0.52 K, C = 1.35 $cm^3\ mol^{-1}\ K$) respectively.

1. Introduction

Coordination polymers assembled by tricyanomethanide (tcm) have attracted great interest because of their fascinating structure characteristics and interesting magnetic properties [1,2]. Due to its three potentially coordinating nitrogen atoms and diverse coordination modes, for example, monodentate, $\mu_{1,5}$, $\mu_{1,5,7}$ and $\mu_{1,1,5,7}$, the tcm ligand has been utilized as a useful "building block" to construct a variety of coordination networks. To date, most binary tcm complexes display a rutile-like structure [3], except that a doubly interpenetrated (6,3) sheet was observed in $Ag(tcm)_2$ [4]. To elucidate the structure–property relationship of tcm complexes, a number of co-ligands such as hexamethylenetetramine, 4,4′-bipyridyl, 1,2-bi(4-pyridyl)ethane or pyrazine were introduced and the structures as well as magnetic properties of the adjusted complexes have been systematically investigated. Among the Cu(I), Ag(I) or Cd(II) tcm complexes with these co-ligands, numerous structure types range from doubly interpenetrated (4,4) sheet, 3D rutile networks to 3D networks with mixed 3- and 5-connecting centers were found [5]. By contrast, modification of the M-tcm binary system (M = Mn(II), Fe(II), Co(II), Ni(II), Cu(II)) with various co-ligands often leads to the formation of chain-like or (4,4) sheet-like structures [6]. However, recently Julve group reported unique structures and interesting magnetic properties of copper tcm complexes with bis(2-pyridyl)pyrazine, 2,2′-bipyrazine and 2,3,5,6-tetrakis(2-pyridyl)pyrazine etc. as co-ligands [7]. On the other hand, to explore how the structure and magnetic properties of modified tcm complexes is affected by the co-ligands, much attempt has been made and several tcm complexes with flexible polyamine [8], di(2-pyridyl)amine [9], 2,2′-bipyrimidine [10], 2,2′:6′,2″-terpyridine [11] and 2,2′-dipyridyl N,N′-dioxide [12] have been structurally and magnetically characterized in our laboratory. In addition, tris(2-aminoethyl)amine (tren) is a novel co-ligand and has four potential nitogen donor atoms, and several new nickel(II) complexes with such co-ligand have been synthesized and characterized [13]. Therefore, introduction of tren co-ligands to binary tcm systems may result in some interesting structures and magnetic properties. However, no transition metal tcm complexes with tren as a co-ligand have ever been reported. As part of our further investigation into the structure and magnetic properties of tcm complexes, we herein report the synthesis and characterization of two new transition metal tcm complexes with tris(2-aminoethyl)amine as co-ligands: $[Ni(tren)(tcm)_2]$ (**1**) and $[Cu(tren)]_3{\cdot}(\mu_3\text{-tren}){\cdot}NO_3{\cdot}5tcm{\cdot}2H_2O$ (**2**).

* Corresponding authors. Tel.: +86 21 81871219x5; fax: +86 21 81871218.
E-mail addresses: liubaoshu@126.com (B.-S. Liu), zhxinrong@163.com (X.-R. Zhang).

http://dx.doi.org/10.1016/j.ica.2014.03.039
0020-1693/

2. Experimental

2.1. Physical measurements

Elemental analyses for C, H and N were performed at Elementar Vario EL-III analyzer. Ni and Cu analyses were made on a Jarrell-Ash 1100 + 2000 inductively coupled plasma quantometer (ICP). Infrared spectra were recorded on a Nicolet FT-170 SX spectrometer with KBr pellets in the 4000–400 cm^{-1} region. Thermogravimetry (TG) analyses for both complexes was performed using PerkinElmer Diamond TG/DTG instruments under nitrogen atmosphere from 25 °C to 1000 °C at a heating rate of 10 °C min^{-1}. The magnetic measurements for **1** and **2** were carried out a Quantum Design MPMS-5 SQUID magnetometer under an applied magnetic field of 3 kOe in the temperature range 2–300 K. Diamagnetic correction was made with Pascal's constants for all constituent atoms and magnetic moments were calculated by the equation $\mu_{eff} = 2.828(\chi_M T)^{1/2}$, where χ_M is the molar magnetic susceptibility corrected for the diamagnetism of the constituting atoms.

2.2. Preparations

$Ni(NO_3)_2{\cdot}6H_2O$, $Cu(NO_3)_2{\cdot}3H_2O$, Tren and $KC(CN)_3$ were purchased from commercial sources and used as received.

2.2.1. [Ni(tren)(tcm)$_2$] (**1**)

A 5 ml ethanol solution of tris(2-aminoethyl)amine (14.6 mg, 0.1 mmol) was added dropwise to a 2 ml aqueous solution of $Ni(NO_3)_2{\cdot}6H_2O$ (29.1 mg, 0.1 mmol) under stirring. To the resulting pale-purple solution was added a 3 ml ethanol–water mixed solution (EtOH:H_2O = 2:1, *V*:*V*) of potassium tricyanomethanide (25.8 mg, 0.2 mmol). After being stirred for another 5 min, the pale-purple solution was filtered and the filtrate was evaporated slowly in air. After 2 weeks, purple block crystals of [Ni(tren)$(tcm)_2$] (**1**) were isolated. Yield 29%. *Anal.* Calc. for $C_{14}H_{18}N_{10}Ni$: C, 43.67; H, 4.71; N, 36.38; Ni, 15.24. Found: C, 43.51; H, 4.84; N, 36.56; Ni, 15.67%.

IR(KBr): *ν*(C≡N) 2232, 2178 cm^{-1}. The infrared C≡N stretch (2232, 2178 cm^{-1}) indicates the coordination of tcm anions to nickel cation [14]. The strong bands at 3326, 3281, 3184 cm^{-1} could be attributed to the N-H stretch of tren ligand, while the band 1271–1112 cm^{-1} also indicates the existence of N-C stretch of tren molecule.

2.2.2. [Cu(tren)]$_3{\cdot}$($_3$-tren)$\cdot NO_3{\cdot}$5tcm$\cdot 2H_2O$ (**2**)

A 5 ml ethanol solution of tris(2-aminoethyl)amine (14.6 mg, 0.1 mmol) was added dropwise to a 2 ml aqueous solution of $Cu(NO_3)_2{\cdot}3H_2O$ (24.2 mg, 0.1 mmol) under stirring. To the resulting blue solution was added a 3 ml ethanol–water mixed solution (EtOH:H_2O = 2:1, *V*:*V*) of potassium tricyanomethanide (25.8 mg, 0.2 mmol). After being stirred for another 5 min, the blue solution was filtered and the filtrate was evaporated slowly in air. After 2 weeks, green–blue block crystals of [Cu(tren)]$_3{\cdot}$(μ_3-tren)$\cdot NO_3$ $\cdot$5tcm$\cdot 2H_2O$ (**2**) were obtained. Yield 31%. *Anal.* Calc. for $C_{44}H_{76}Cu_3N_{32}O_5$: C, 39.92; H, 5.79; N, 33.86; Cu, 14.40. Found: C, 39.78; H, 5.91; N, 34.02; Cu, 14.92%.

IR(KBr): *ν*(C≡N) 2173 cm^{-1}. The infrared C≡N stretch (2173 cm^{-1}) reveals that the tcm anions is free in **2**. The strong bands at 3336, 3249, 3164 cm^{-1} may be due to the N–H stretch of tren ligand, while the band 3493–3408 cm^{-1} also suggests the existence of O–H stretch of water molecule, and the bands at 1397, 1362 cm^{-1} indicates the presence of the ionic nitrate in the complex.

Table 1
Crystal data and structure refinement for **1** and **2**.

	1	**2**
Formula	$C_{14}H_{18}N_{10}Ni$	$C_{44}H_{76}Cu_3N_{32}O_5$
Formula weight	385.09	1323.99
Crystal system	orthorhombic	monoclinic
Space group	*P*2(1)2(1)2	*P*2(1)/c
a (Å)	14.523(5)	16.129(7)
b (Å)	15.298(5)	25.55(1)
c (Å)	8.178(3)	17.250(8)
α (°)	90	90
β (°)	90	115.742(6)
γ (°)	90	90
V (Å^3)	1817(1)	6403(5)
Z	4	4
D_{calc} (gm cm^{-3})	1.408	1.373
μ (Mo Kα) (mm^{-1})	1.087	1.055
Total/unique data	8678/3881	28 629/12514
Observed data [$I > 2\sigma(I)$]	3546	7827
R_{int}	0.0470	0.0471
R_1, wR_2 [$I > 2\sigma(I)$]	0.0347/0.0811	0.0388/0.0857
R_1, wR_2 (all data)	0.0380/0.0826	0.0702/0.0929

2.3. Crystallography

Data collection for **1** and **2** was carried out on a Bruker Smart APEX CCD diffractometer equipped with graphite monochromated MoKα radiation (λ = 0.71073 Å) at 298 K. Intensities were corrected for empirical absorption based on an SADABS scan technique [15]. The structures were solved by direct methods using SHELXS-97 program and refined by full-matrix least-squares on F^2 using SHELXL-97 program [16]. All non-H atoms were refined anisotropically, and the H atoms attached to C atoms and N atoms were added at calculated positions with the distances of C–H bond (0.9700 Å) and N–H bond (0.9000 Å) respectively, while the positions of water H atoms are found in difference Fourier map and refined with the distances of O–H bond range from 0.72(3) to 0.96(2) Å.

Crystallographic data of the two complexes are given in Table 1. Selected bond distances of **1** and **2** are in Tables 2 and 3, respectively. Selected bond angels of **1** and **2** are in Tables S1 and S2, respectively. Hydrogen bond parameters of **1** and **2** are in Table S3 and S4, respectively.

3. Results and discussion

3.1. Synthesis and crystal structure

The reaction of nickel nitrate, tris(2-aminoethyl)amine and potassium tricyanomethanide at a 1:1:2 M ratio in the mixed solvent of water and ethanol (H_2O:C_2H_5OH = 3:7) resulted in the

Table 2
Selected bond distances (Å) for **1**.

Ni(1)–N(5)	2.049(2)	Ni(1)–N(2)	2.106(2)
Ni(1)–N(4)	2.080(2)	Ni(1)–N(3)	2.119(2)
Ni(1)–N(1)	2.085(2)	Ni(1)–N(8)	2.127(2)

Table 3
Selected bond distances (Å) for **2**.

Cu(1)–N(2)	2.003(2)	Cu(2)–N(10)	2.085(2)
Cu(1)–N(7)	2.044(2)	Cu(2)–N(11)	2.088(2)
Cu(1)–N(5)	2.048(2)	Cu(3)–N(4)	2.000(2)
Cu(1)–N(6)	2.090(2)	Cu(3)–N(13)	2.049(2)
Cu(1)–N(8)	2.119(2)	Cu(3)–N(14)	2.071(2)
Cu(2)–N(3)	2.005(2)	Cu(3)–N(15)	2.077(3)
Cu(2)–N(9)	2.059(2)	Cu(3)–N(16)	2.081(2)
Cu(2)–N(12)	2.066(2)		