ЖУРНАЛ СТРУКТУРНОЙ ХИМИИ

2017. Том 58, № 3 *Март – апрель* *С. 650 – 651*

КРАТКИЕ СООБЩЕНИЯ

UDC 548.73:541.49:546.96

CRYSTAL STRUCTURE OF A DINUCLEAR NITRIDO-BRIDGED RUTHENIUM COMPLEX WITH PYRIDINE LIGANDS

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Received July, 30, 2015 *Revised — August, 27, 2015*

A new dinuclear nitrido-bridged ruthenium complex with pyridine ligands ([PyH][$Ru_2N(Py)_4Cl_6$] (**1**) is synthesized by reacting $K_3[Ru_2NCl_8(H_2O)_2]$ (**2**) and excessive pyridine, then crystallized from dilute hydrochloric acid. Its crystal structure is determined by single crystal X-ray diffraction. The complex crystallizes in the form of red block crystals of the monoclinic symmetry and the space group *C*2. The nitrido-bridged ruthenium complex has very short Ru—N distances.

DOI: 10.15372/JSC20170329

K e y w o r d s: dinuclear, ruthenium complex, nitrido-bridged, pyridine, crystal structure.

Dinuclear μ-nitrido complexes of ruthenium are the most promising plating salts for electrodeposited ruthenium. $K_3[Ru_2NX_8(H_2O)_2]$ (X = Cl or Br) belonging to this category has been widely used in the electrical contact application due to its high stability [1, 2]. Cleare and Griffith [3] have shown the formula of the compounds based on the spectroscopic data. Ciechanowicz and Skapski [4] obtained the crystal structure of $K_3[Ru_2NCl_8(H_2O)_2]$. To the best of our knowledge, dinuclear μ-nitrido complexes of ruthenium are still rare [5].

In this contribution, we present the synthesis and crystal structure of a new dinuclear nitrido-ruthenium complex with pyridine ligands.

Experimental. Synthesis of [PyH][$Ru_2N(Py)_4Cl_6$] (1). $K_3[Ru_2NCl_8(H_2O)_2]$ (0.26 g, 0.40 mmol) was dissolved in 5 ml of water and filtered through a 0.25 μm membrane to produce a clear solution to which pyridine (0.63 g, 8 mmol) was added. The mixture solution was stirred and heated to reflux for 30 min, and then dilute hydrochloric acid (10 ml, 1 mol/L) was added. The insoluble substance was filtered off. The filtrate obtained was slowly cooled to room temperature and a red crystalline product appeared within two weeks with a 91 % (0.30 g) yield. Anal. Calcd. for $C_{25}H_{26}Cl_6N_6Ru_2$ (825.36): C 36.31, H 3.14, N 10.15. Found: C 36.34, H 3.15, N 10.18.

X-ray diffraction analysis. Single crystals of **1** were obtained as described above. Intensity data for the single crystal (size 0.31×0.26×0.18 mm) was collected at room temperature on BRUKER SMART APEX II equipped with a CCD detector using graphite monochromatized MoK_α radiation (λ = 0.071073 nm) in the θ range from 2.37° to 25.0°. In total, 4798 reflections were measured. Crystallographic data: a = 13.314(2) Å, b = 12.407(2) Å, c = 10.9880(17) Å, β = 116.119(2)°, space group *C*2, V = 1629.7(5) Å^3, Z = 2, d_{calc} = 1.682 g/cm^3. The crystal structure was solved by the direct method. The crystalline phase has the composition $C_{25}H_{26}Cl_6N_6Ru_2$. The final full-matrix refinement on 2735 independent reflections led to R_1 = 0.0695 (wR_2 = 0.1512). For 2334 reflections with $I > 2\sigma(I)$:

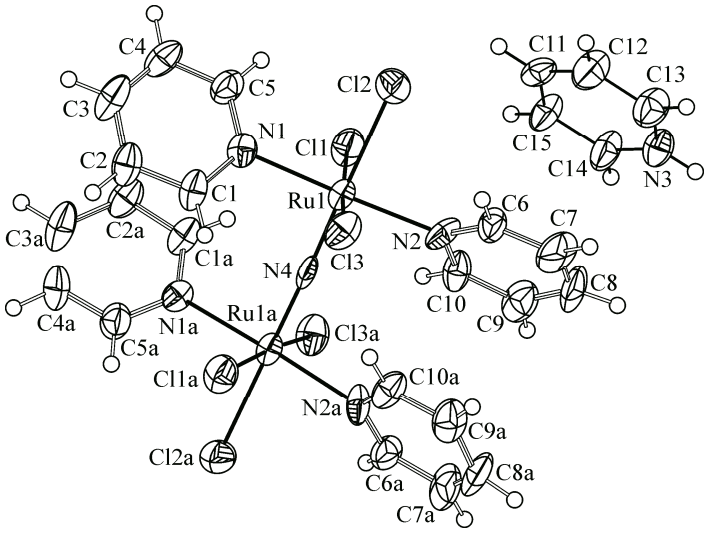

Fig. 1. ORTEP diagram of **1** displaying thermal ellipsoids at a 30 % probability

Table 1

Selected bond lengths (Å) *and angles* (deg.) *for* **1**

Ru(1)—Cl(1)	2.387(3)
Ru(1)—Cl(3)	2.384(2)
Ru(1)—N(2)	2.098(10)
Ru(1)—Cl(2)	2.440(2)
Ru(1)—N(1)	2.124(9)
Ru(1)—N(4)	1.7376(8)
Ru(1)#1—N(4)—Ru(1)	178.4(11)
N(4)—Ru(1)—N(1)	91.5(6)
N(4)—Ru(1)—Cl(3)	92.84(13)
N(1)—Ru(1)—Cl(3)	89.9(3)
N(2)—Ru(1)—Cl(1)	88.6(3)
Cl(3)—Ru(1)—Cl(1)	173.97(10)
N(2)—Ru(1)—Cl(2)	89.1(3)
Cl(3)—Ru(1)—Cl(2)	86.78(10)
N(4)—Ru(1)—N(2)	90.5(6)
N(2)—Ru(1)—N(1)	177.6(4)
N(2)—Ru(1)—Cl(3)	91.3(3)
N(4)—Ru(1)—Cl(1)	93.19(13)
N(1)—Ru(1)—Cl(1)	89.9(3)
N(4)—Ru(1)—Cl(2)	179.5(5)
N(1)—Ru(1)—Cl(2)	88.9(2)
Cl(1)—Ru(1)—Cl(2)	87.19(10)

$R_1 = 0.0577$ ($wR_2 = 0.1451$). The *S*-factor against F^2 is 1.013. All calculations were made using the SHELXTL-97 software [6]. The CIF files with complete information about the structure have been deposited with CCDC No. 1414333 for **1**, from which it is available free of charge on request at www.ccdc.cam.ac.uk/data_request/cif.

Results and discussion. Complex **1** was prepared by refluxing complex **2** with excessive pyridine. Compound **1** crystallizes from dilute hydrochloric acid. Complex **1** crystallized in the space group *C*2 and the monoclinic crystal system. The structure as determined from single crystal X-ray diffraction studies is shown in Fig. 1. As shown in Fig. 1, it is a dinuclear nitrido-bridged ruthenium complex. The Ru atom lying on mirror planes adopts a distorted octahedral coordination geometry with two pyridine N atoms, three chlorine atoms, and a μ-nitrido N atom. The structure contains the $[Ru_2N(Py)_4Cl_6]^-$ ion which has the 2/*m* crystallographic symmetry, with the bridging nitrogen atom lying in the center of symmetry. Selected bond lengths and angles are listed in Table 1. In complex **1**, the Ru—Cl bond lengths are in the range 2.384—2.440 Å, Ru—N (Py) bond lengths are 2.124 and 2.098 Å; these bond distances agree with the literature [7] data regarding $[Ru(NH_3)_5Cl](NO_3)_2$. However, the Ru—N—Ru bridge is very short with Ru—N distances of 1.7376 Å, and the Ru—N—Ru bond angle of 178.4°. Therefore there is the multiple bonding with a considerable π-character [4].

This work was supported by the Provincial Science and Technology Development Programs of Yunnan (Grant No. 2015IB019, 2016FB291) and the Key Technology Development Project of Kunming City.

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