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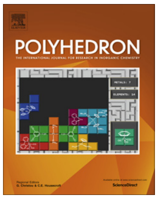

Synthesis, crystal structure and MMCT of a heterobimetallic cyanide-bridged complex *trans*-BrRu^{II}(dppe)$_2$(μ-CN)(Fe^{III}Br$_3$)

Ming Liu, Jianmei Hu, Yong Wang *

College of Chemical Engineering and Pharmacy, Jingchu University of Technology, Jingmen, Hubei 444800, PR China

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ABSTRACT

The syntheses, crystal structures, IR and electronic absorption spectroscopy of cyanide-bridged complex *trans*-BrRu^{II}(dppe)$_2$(μ-CN)(Fe^{III}Br$_3$) (**2**) and its parent *trans*-ClRu^{II}(dppe)$_2$(CN) (**1**) were reported. The crystals crystallized in the monoclinic space group *C*2/*c* for **1**, and monoclinic space group *P*2$_1$/*c* for **2**. The crystal structural data, MMCT (metal-to-metal charge transfer) in electronic absorption spectra and EPR spectra indicate the existence of some electron delocalization along Fe^{III}—NC—Ru^{II} in complex **2**. The magnetic properties of complex **2** were measured and analyzed.

1. Introduction

In the past few decades, considerable efforts have been focused on the design and synthesis of polynuclear complexes due to their interesting magnetic properties and fascinating catalytic, electronic, and photophysical properties [1–5]. Among these complexes, cyanide-bridged complexes have always been the hot topics of the chemists due to their intriguing architectures and promising potential applications in many fields as the cyanide bridge can efficiently mediate strong magnetic interactions between paramagnetic metal ions [6–9]. So far, the research has been focused on the cyanide-bridged polynuclear compounds that two paramagnetic metal ions directly through the cyanide bridge and their magnetic properties [10–15]. However the cyanide-bridged polynuclear compounds that two paramagnetic metal ions separated by diamagnetic cyanidometal bridge is still very rare, mainly due to the distant (more than 1 nm) magnetic interaction is weak or even completely disappear. Therefore, the design and synthesis of such polynuclear compounds with strong magnetic interactions is still a challenge.

Until now, we have synthesized a series of cyanide-bridged complexes that two paramagnetic metal ions are separated by diamagnetic cyanidometal bridge and the cyanide N-bonding Fe^{III} ions are low-spin [16–18]. Meanwhile, we would like to investigate the distant magnetic interaction when the cyanide N-bonding Fe^{III} ions are high-spin. In this item, we report the syntheses, crystal structures and electronic absorption spectra of cyanide-bridged complex *trans*-BrRu^{II}(dppe)$_2$(μ-CN)(Fe^{III}Br$_3$)$_2$ (**2**) and its parent *trans*-ClRu^{II}(dppe)(CN) (**1**).

2. Experimental

2.1. Physical measurements

Elemental analyses (C, H, N) were carried out on a Vario MICRO elemental analyzer. Infrared (IR) spectra were recorded on a Vertex 70 FT-IR spectrophotometer using KBr pellets. Electronic absorption spectra were measured on a Perkin–Elmer Lambda 35 UV–Vis spectrophotometer. EPR studies were performed recorded using a Bruker ELEXSYS E500 spectrometer operating at 9.867826 GHz, 20 mW microwave power, 100 kHz modulation frequency. Magnetic susceptibilities were carried out using a Quantum Design Magnetic Property Measurement System (MPMS) SQUID-XL magnetometer. Diamagnetic correction for complex **2** was made using Pascal's constants.

2.2. Materials

All manipulations were performed under argon atmosphere with the use of standard Schlenk techniques unless otherwise stated. CH_2Cl_2 was dried by distillation over calcium hydride and $CH_3CH_2OCH_2CH_3$ was dried by distillation over sodium wire under argon atmosphere. CH_3OH was dried by distillation over magnesium. *trans*-Ru^{II}(dppe)$_2$Cl$_2$ [19,20] was prepared according to the

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* Corresponding author.
E-mail address: wangyong198711@yahoo.com (Y. Wang).

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literature procedures. All other reagents were available commercially and used without further purification.

2.3. *trans*-ClRu^{II}(dppe)$_2$(CN)·C_3H_7NO, 1·C_3H_7NO

Under argon atmosphere, a solution of *trans*-Ru^{II}(dppe)$_2$Cl$_2$ (969 mg, 1.0 mmol) in CH_2Cl_2 (50 ml) was mixed with KCN (1300 mg, 20 mmol) in H_2O (20 ml). The mixture was refluxed for 3 h, and then cooled to room temperature. The organic layer was separated and the aqueous residue was extracted with CH_2Cl_2 (3 × 20 ml). The combined organic extracts were dried over anhydrous $MgSO_4$, concentrated and dried in vacuum to give the desired product as a yellow solid. 50 mL of DMF-CH_3OH solution (1:9, V/V) was added to this solid stirring for 10 min. The resulting yellow solution was filtered and the insoluble part of the residue was discarded. Yellow crystals of **1** (650 mg, 63%), suitable for crystallographic studies were formed after one month by slow evaporation at room temperature. *Anal.* Calc. for $C_{56}H_{55}ClN_2OP_4Ru$: C, 65.15; H, 5.37; N, 2.71. Found: C, 65.27; H, 5.25; N, 2.53%. IR (KBr pellet, cm^{-1}): 3092w, 3077w, 3052s, 3002w, 2982w, 2963w, 2922w, 2068s, 1677s, 1586w, 1566w, 1553w, 1502w, 1485w, 1430s, 1408w, 1381m, 1315w, 1261w, 1195m, 1159m, 1094s, 1025m, 998m, 915w, 879m, 842w, 808s, 743s, 693s, 668m, 643m, 616w, 531s, 507s. UV–Vis (CH_3CN), λ_{max}, nm (ε, dm^3 mol^{-1} cm^{-1}): 359 (800).

2.4. *trans*-BrRu^{II}(dppe)$_2$(μ-CN)(Fe^{III}Br$_3$)·CH_2Cl_2, 3·CH_2Cl_2

Under argon atmosphere, a solution of **1** (103.2 mg, 0.10 mmol) in CH_2Cl_2 (10 ml) was mixed with Fe^{III}Br$_3$ (44.4 mg, 0.15 mmol) in CH_3OH (10 ml). The resulting solution was stirred at 35 °C for 3 h. The solvent was removed and CH_2Cl_2 (20 ml) was added to the resultant solid. The reaction mixture was filtered and the filtrate was concentrated under reduced pressure. The resultant residue was dissolved in a mixed solution of CH_2Cl_2 and $CH_3CH_2OCH_2CH_3$ (1:3, *V*/*V*, 40 ml) at room temperature to give **2** as red crystals (88.6 mg, 64%). *Anal.* Calc. for $C_{54}H_{50}Br_4Cl_2FeNP_4Ru$: C, 46.85; H, 3.64; N, 1.01. Found: C, 46.58; H, 3.64; N, 1.24%. IR (KBr pellet, cm^{-1}): 3080w, 3050m, 3022w, 3002w, 2986w, 2949w, 2918w, 1984s, 1584w, 1568w, 1543w, 1523w, 1510w, 1501w, 1485m, 1431s, 1403w, 1383w, 1307m, 1258m, 1191m, 1154m, 1094s, 1023m, 1000m, 919w, 876m, 843w, 823m, 805w, 740s, 695s, 670w, 643w, 532m, 506 m. UV–Vis (CH_3CN), λ_{max}, nm (ε, dm^3 mol^{-1} cm^{-1}): 334(1881), 427(1596), 642(1338).

2.5. X-Ray crystal structure determination

Single crystal X-ray crystallographic data of complexes **1** and **2** were collected on a Saturn724+ CCD diffractometer equipped with graphite-monochromatic Mo K_α (λ = 0.71073 Å) radiation using an ω scan mode at 123 K. The structure was solved by the direct methods with SHELXL-*2016* [21] program and refined by full-matrix least-squares (SHELXL-*2016*) on F^2. Anisotropic thermal parameters were used for the non-hydrogen atoms, and isotropic parameters were used for the hydrogen atoms. Hydrogen atoms were added geometrically and refined using a riding model. The detail crystallographic data for **1** and **2** are summarized in Table 1. Selected bond lengths and bond angles for **1** and **2** are listed in Table 2.

Table 1
Crystallographic data and details of structure determination for complexes **1** and **2**.

Complex	**1**·C_3H_7NO	**2**·CH_2Cl_2
Chemical formula	$C_{56}H_{55}ClN_2OP_4Ru$	$C_{54}H_{50}Br_4Cl_2FeNP_4Ru$
Formula weight	1032.42	1384.29
Colour and Habit	white prism	red prism
Crystal size (mm)	0.461 × 0.440 × 0.117	0.290 × 0.183 × 0.171
T (K)	123	123
Crystal system	monoclinic	monoclinic
Space group	*C*2/*c*	*P*2$_1$/*c*
a (Å)	28.027(5)	13.986(10)
b (Å)	14.1473(12)	25.112(16)
c (Å)	12.701(2)	19.182(10)
α (°)	90.00	90.00
β (°)	105.430(8)	125.94(4)
γ (°)	90.00	90.00
V (Å^3)	4854.4(12)	5455(6)
Z	4	4
ρ_{calcd} (g/cm^3)	1.413	1.686
λ (Mo K_α, Å)	0.71073	0.71073
μ (Mo K_α, mm^{-1})	0.553	3.725
Completeness	96.7%	99.8
F(000)	2136	2740
h, *k*, *l*, range	$-34 \le h \le 36$, $-18 \le k \le 18$, $-16 \le l \le 13$	$-18 \le h \le 18$, $-32 \le k \le 32$, $-24 \le l \le 24$
θ range (°)	2.46–27.48	2.42–27.50
Reflections measured	5396	12477
R_{int}	0.0340	0.1124
Params/restraints/ Data(obs.)	324/19/5151	592/123/6909
Goodness-of-fit (GOF) on F^2	1.076	1.014
R_1, $_\omega R_2$ (I > 2σ(*I*))	0.0406, 0.1084	0.0720, 0.1790
R_1, $_\omega R_2$ (all data)	0.0422, 0.1099	0.0952, 0.2025

Table 2
Selected bond lengths (Å) and bond angles (°) for complexes **1** and **2**.

Complex	**1**	**2**
Ru—C	1.844(2)	1.917(7)
Ru—Cl (Br)	2.548(2)	2.572 (2)
Ru1—P1	2.3670(5)	2.413(2)
Ru1—P2	2.3884(6)	2.392(2)
Ru1—P3		2.389(2)
Ru1—P4		2.393(2)
C≡N	1.240(3)	1.172(9)
C—Ru—C(Br)	180.0	174.9(2)
N≡C—Ru	176.9(9)	174.4(6)
C≡N—Fe		175.9(6)
Fe—N1		1.922(6)
Fe—Br1		2.316(2)
Fe—Br2		2.314(2)
Fe—Br3		2.320(2)
Fe···Ru		5.006
Fe···Fe(intermolecular)		8.526
Ru···Fe(—NC—)		5.012

3. Results and discussion

3.1. Synthesis

Complex **1** was obtained in a similar way to our previous report [22], which is refluxed of *trans*-Ru^{II}(dppe)$_2$Cl$_2$ in CH_2Cl_2 with extremely excess KCN (20 equiv.) in H_2O over a period of 3 h. Compound **1** has ν_{CN} band at 2068 cm^{-1}. Complex **2** was prepared in a straightforward way by reaction of or *trans*-Ru^{II}(dppe)$_2$(CN)$_2$ in CH_2Cl_2 with Fe^{III}Br$_3$ in CH_3OH under ambient condition. The IR spectra show the ν_{CN} stretching band at 1984 cm^{-1} for **2**. This is because the π back-bonding from the carbon-bound metal (Ru^{II}) into the CN bond is enhanced when the cyanide is coordinated to the electron-attracting metal Fe^{III} ions, leading to a weakening of the C≡N bond and hence a shift to lower frequency for CN is expected [23,24].

3.2. Description of the crystal structures of **1** and **2**

The structural drawings of complexes **1** and **2** are shown in Figs. 1 and 2. The crystals crystallize in the monoclinic space group