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Synthesis, crystal structures and catalytic activity of tetrakis(acetato)dirhodium(II) complexes with axial picoline ligands

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ABSTRACT

Three complexes were synthesized in high yields by reaction of $Rh_2(O_2CCH_3)_4$ with 2-picoline (**1**), 3-picoline (**2**) and 4-picoline (**3**), respectively, and characterized by elemental analysis, ESI^+-MS, FT-IR and ^1H NMR along with single-crystal X-ray structural analysis. All picoline ligands coordinate to the axial sites of $Rh_2(O_2CCH_3)_4$ via the pyridine nitrogen atoms, and interestingly, the coordination of 2-picoline in **1** is assisted by two intramolecular C–H···O hydrogen bonds formed between the methyl of 2-picoline and the oxygen atoms of $Rh_2(O_2CCH_3)_4$. Moreover, the intermolecular C–H···O interactions play the main role in the structural stacking of **1**–**3**. Their catalytic activity was evaluated in the C–H insertion reactions for the preparation of 4-nitrobenzyl-(4R,5R,6S)-6-((R)-1-hydroxyethyl)-4-methyl-3,7-dioxo-1-azabicyclo [3.2.0] heptane-2-carboxylate, a key intermediate of Meropenem. The isolated yields for **1**, **2** and **3** are 44%, 16% and 22%, respectively, significantly lower than the value of $Rh_2(O_2CCH_3)_4$ (73%), indicating that the axial ligands have negative but different influence on the catalytic activity. The activities of **1**–**3** are related to the displacement rate of the axial ligands, and essentially related to the Rh–N bond lengths which strong affect the displacement rate. Therefore, it is possible to tune the catalytic activity of $Rh_2(O_2CCH_3)_4$ by changing its axial ligands.

1. Introduction

Dirhodium(II) tetracarboxylates of type $Rh_2(O_2CR)_4L_2$, in which the four carboxylates (the equatorial ligands) bridge the two rhodium atoms and L represents a Lewis base (the axial ligands) bound to the Rh–Rh axis, have attracted considerable attention in recent years due to their potential applications as catalysts [1–6], antitumor agents [7–13] and building blocks for supramolecular arrays [14–16]. Dirhodium(II) tetracarboxylates are quite stable and can be used to construct various new derivatives via equatorial ligand substitution or axial ligand exchange [16,17]. The equatorial ligand substitution usually takes place at reflux in high boiling-point solvents, while the axial ligand exchange reaction can quickly occur at room temperature. This different reactivity resulted in the isolation of several dirhodium(II) tetracarboxylates and large amounts of axial adducts [16–18]. Among these adducts, the axial ligands are mostly nitrogenous heterocyclic compounds. Typical examples of this type of ligands are pyridine and its derivatives. The adducts, formed by reaction of pyridine and its derivatives with dirhodium(II) tetracarboxylates, have been extensively investigated since the discovery the paddlewheel structure of dirhodium(II) tetraacetate [17,18]. However, it is surprising that the picoline adducts of dirhodium(II) tetracarboxylates have not been systemically explored up to now, although picoline is an obvious derivative of pyridine. In this context, we report the characterization, crystal structures and catalytic activity of three picoline adducts of dirhodium(II) tetraacetate.

2. Experimental

2.1. General

Tetrakis(acetato)dirhodium(II) ($Rh_2(O_2CCH_3)_4$) was prepared using literature procedure [19]. (3S,4R)-3-[(1R)-1-Hydroxyethyl]-

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Table 1
Crystal data and structural refinements for **1**–**3**.

	1	**2**	**3**
Empirical formula	$C_{20}H_{26}N_2O_8Rh_2$	$C_{20}H_{26}N_2O_8Rh_2$	$C_{20}H_{26}N_2O_8Rh_2$
M_r	628.25	628.25	628.25
T (K)	100(2)	100(2)	100(2)
λ (Å)	0.71073	0.71073	0.71073
Crystal system	monoclinic	triclinic	monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$
a (Å)	7.6476(12)	7.7224(8)	10.4429(13)
b (Å)	19.930(3)	8.2418(9)	12.9252(16)
c (Å)	8.2011(13)	10.6156(11)	8.8736(11)
α (°)	90	77.661(1)	90
β (°)	115.963(2)	71.673(1)	101.897(2)
γ (°)	90	62.427(1)	90
V (Å^3)	1123.8(3)	566.66(10)	1172.0(3)
Z	2	1	2
D_{calc} (g cm^{-3})	1.857	1.841	1.780
μ (mm^{-1})	1.517	1.505	1.455
F(000)	628	314	628
Crystal size (mm^3)	0.28 × 0.09 × 0.04	0.23 × 0.20 × 0.04	0.13 × 0.13 × 0.06
θ range (°)	2.04–27.99	2.03–27.99	1.99–28.00
Limiting indices	$-10 \leqslant h \leqslant 10$, $-26 \leqslant k \leqslant 25$, $-10 \leqslant l \leqslant 10$	$-10 \leqslant h \leqslant 10$, $-10 \leqslant k \leqslant 10$, $-14 \leqslant l \leqslant 13$	$-13 \leqslant h \leqslant 13$, $-17 \leqslant k \leqslant 17$, $-11 \leqslant l \leqslant 11$
Reflection collected	10,657	7351	11,286
Independent reflection (R_{int})	2704 (0.0410)	2707 (0.0243)	2816 (0.0494)
Max. and min. transmission	0.9418 and 0.6760	0.9423 and 0.7235	0.9178 and 0.8334
Data/restraints/parameters	2704/0/146	2707/0/233	2816/0/148
Goodness-of-fit (GOF) on F^2	1.048	1.071	1.014
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0312, wR_2 = 0.0650	R_1 = 0.0243, wR_2 = 0.0598	R_1 = 0.0300, wR_2 = 0.0644
R indices (all data)	R_1 = 0.0449, wR_2 = 0.0692	R_1 = 0.0284, wR_2 = 0.0621	R_1 = 0.0504, wR_2 = 0.0709
$\Delta\rho_{max/min}$ (e Å^{-3})	1.008/−0.838	0.586/−1.270	0.762/−0.650

4-[(1R)-1-methyl-3-diazo-3-(*p*-nitrobenzyloxycarbonyl)-2-oxo-propyl]azetidin-2-one (**4**) was purchased from Sigma–Aldrich Co. Ltd. All chemicals and solvents were used as received without further purification, unless otherwise stated. Elemental analyses for C, H and N were performed with a Carlo-Erba Instrument. Electrospray ionization mass spectra (ESI-MS) studies were carried out on an Agilent G6230 Spectrometer. FT-IR spectra were recorded in the 4000–400 cm^{-1} region on a Bruker Tensor 27 Spectrometer with KBr pellets. ^{1}H and ^{13}C NMR spectra were obtained on a Bruker Avance 400 spectrometer with TMS as an internal standard. Melting points were determined on a Thomas Hoover capillary melting point apparatus and were uncorrected. Optical rotations were measured with a Perkin–Elmer 240 polarimeter. UV–Vis spectra were recorded on a Varian Cary 50 spectrophotometer equipped with a PCB-150 water circulator. Column chromatography was performed on silica gel (200–300 mesh).

2.2. Synthesis

Complexes **1**–**3** were prepared by a similar procedure. In general, an aqueous solution (30 mL) of $Rh_2(O_2CCH_3)_4$ (0.031 g, 0.07 mmol) was placed in a Schlenk tube. After an ethanol aqueous solution (1:1 v/v, 10 mL) was carefully layered on the previous solution as a middle layer, an ethanol solution (10 mL) of picoline (0.052 g, 0.56 mmol) was put onto the layer. The tube was left undisturbed for one week to yield pink single crystals. The crystals were collected on a frit, washed with water and ethanol, and dried in vacuo.

2.2.1. $Rh_2(O_2CCH_3)_4(2\text{-}CH_3\text{-}C_5H_4N)_2$ (**1**)

Yield: 41 mg (93%). *Anal.* Calc. for $C_{20}H_{26}N_2O_8Rh_2$: C, 38.24; H, 4.17; N, 4.46. Found: C, 38.0; H, 4.1; N, 4.4%. ESI$^+$-MS (in MeOH) m/z: 465, [M − 2Picoline + Na]$^+$; 506, [M − 2Picoline + 2CH$_3$OH]$^+$; 907, [2 M − 4Picoline + Na]$^+$. IR (KBr): 3026 (w), 2988 (w), 2935 (w), 1593 (vs), 1486 (m), 1434 (vs), 1345(m), 1308(m), 772 (m), 699 (s). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.49 (br s, 2H, Py-*H*), 7.71 (br s, 2H, Py-*H*), 7.24 (br, 4H, Py-*H*), 2.49 (s, Py-*CH*$_3$, overlapped with the methyl of DMSO), 1.79 (s, 12H, 4*CH*$_3$COO).

2.2.2. $Rh_2(O_2CCH_3)_4(3\text{-}CH_3\text{-}C_5H_4N)_2$ (**2**)

Yield: 40 mg (91%). *Anal.* Calc. for $C_{20}H_{26}N_2O_8Rh_2$: C, 38.24; H, 4.17; N, 4.46. Found: C, 38.2; H, 4.1; N, 4.3%. ESI$^+$-MS (in MeOH) m/z: 465, [M − 2Picoline + Na]$^+$; 506, [M − 2Picoline + 2CH$_3$OH]$^+$; 558, [M − Picoline + Na]$^+$; 907, [2 M − 4Picoline + Na]$^+$; 1000, [2 M − 3Picoline + Na]$^+$. IR (KBr): 3017 (w), 2983 (w), 2928 (w), 1591 (vs), 1481 (m), 1433 (vs), 1345 (m), 792 (m), 706 (s). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.94 (br, 2H, Py-*H*), 8.42 (br, 2H, Py-*H*), 7.63 (br, 2H, Py-*H*), 7.32 (br, 2H, Py-*H*), 2.32 (s, Py-*CH*$_3$, partially overlapped with the methyl of DMSO), 1.77 (s, 12H, 4*CH*$_3$COO).

2.2.3. $Rh_2(O_2CCH_3)_4(4\text{-}CH_3\text{-}C_5H_4N)_2$ (**3**)

Yield: 41 mg (93%). *Anal.* Calc. for $C_{20}H_{26}N_2O_8Rh_2$: C, 38.24; H, 4.17; N, 4.46. Found: C, 37.9 H, 4.1; N, 4.4%. ESI$^+$-MS (in MeOH) m/z: 465, [M − 2Picoline + Na]$^+$; 506, [M − 2Picoline + 2CH$_3$OH]$^+$; 558, [M − Picoline + Na]$^+$; 599, [M − Picoline + 2CH$_3$OH]$^+$; 907, [2 M − 4Picoline + Na]$^+$; 1000, [2 M − 3Picoline + Na]$^+$; 1093, [2 M − 2Picoline + Na]$^+$. IR (KBr): 3013 (w), 2985 (w), 2921 (w), 1592 (vs), 1498 (m), 1432 (vs), 1348 (m), 818 (m), 697 (s). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.44 (br, 4H, Py-*H*), 7.21 (br s, 4H, Py-*H*), 2.32 (s, Py-*CH*$_3$, partially overlapped with the methyl of DMSO), 1.77 (s, 12H, 4*CH*$_3$COO).

2.3. Preparation the sample solutions for UV–Vis analysis

UV–Vis signals of **1**–**3** in the range 350–700 nm were recorded in three solvents, dimethyl sulfoxide (DMSO), methanol and ethyl acetate. For the DMSO solutions, each complex (10 mg, for **1**, **2**, **3** or $Rh_2(O_2CCH_3)_4$) was suspended in 10 mL of DMSO, then the resulting mixtures were stirred at room temperature. Complex **1**