Synthesis and Crystal Structure of a Chain Complex of Rhodium(II) Acetate and 1,2-Bis(4-pyridyl)ethane having an N_2 -Adsorption Property

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The title compound, a chain adduct of rhodium(II) acetate with 1,2-bis(4-pyridyl)ethane (bpe), catena(tetrakis(μ -acetato- O, O')(μ -1,2-bis(4-pyridyl)ethane- N, N')dirhodium(II)-water (1/2)), $[\text{Rh}_2(\text{CH}_3\text{CO}_2)_4(\text{bpe})]_n \cdot 2n\text{H}_2\text{O}$, was isolated. The crystal structure was determined by the single-crystal X-ray diffraction method at 293 K. It crystallizes in the monoclinic space group $C2/c$ with $a = 24.937(5)\text{\AA}$, $b = 13.211(3)\text{\AA}$, $c = 8.8480(19)\text{\AA}$, $\beta = 94.189(3)^\circ$, $V = 2907.0(11)\text{\AA}^3$, $D_x = 1.513\text{ g/cm}^3$, and $Z = 4$. The $R1$ [$I > 2\sigma(I)$] and $wR2$ (all data) values are 0.0356 and 0.0863, respectively, for all 3324 independent reflections. The molecule has a linear chain with an alternating arrangement of $\text{Rh}_2(\text{CH}_3\text{CO}_2)_4$ [$\text{Rh}-\text{Rh}$ 2.3990(8) $\text{\AA}$] and bpe. The specific surface area estimated from a N_2 adsorption isotherm was $65.6\text{ m}^2\text{ g}^{-1}$.

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There has been considerable interest in the molecular assembly of metal carboxylates with a lantern-like structure, because such complexes may have an adsorption property for small gas molecules.¹⁻⁴ We have engaged in synthetic studies on rhodium(II) carboxylates with N, N' -bidentate ligands to make molecular assembled systems.⁵⁻⁹ 1,2-Bis(4-pyridyl)ethane (bpe) is an interesting bidentate ligand used to make such compounds, because it has two binding sites with an ethane-type orientation. In this study, we isolated an adduct from a reaction of rhodium(II) acetate and bpe, and determined the crystal structure of this adduct, which is the first example of a bpe adduct of rhodium(II) acetate, as shown in Fig. 1. The adsorption property was examined for N_2 .

Rhodium(II) acetate was prepared by a method described in

the literature.⁵ A 6.4 mg (0.035 mmol) portion of bpe was added to a solution of rhodium(II) acetate (10.0 mg, 0.0266 mmol) in 4 cm^3 of ethanol, and the solution was stirred overnight. The precipitate was collected, washed by ethanol, and dried under a vacuum. Yield, 11.7 mg (82%). *Anal.* Found: C, 38.08; H, 4.10; N, 4.58%. Calcd for

Fig. 1 Chemical structure of the title compound.

Table 1 Crystal and experimental data

Chemical formula: $\text{C}_{20}\text{H}_{28}\text{N}_2\text{O}_{10}\text{Rh}_2$	
Formula weight = 662.26	
$T = 293\text{ K}$	
Crystal system: monoclinic	Space group: $C2/c$
$a = 24.937(5)\text{\AA}$	
$b = 13.211(3)\text{\AA}$	$\beta = 94.189(3)^\circ$
$c = 8.8480(19)\text{\AA}$	
$V = 2907.0(11)\text{\AA}^3$	$Z = 4$
$D_x = 1.513\text{ g/cm}^3$	
Radiation: $\text{Mo K}\alpha$ ($\lambda = 0.71073\text{ \AA}$)	
$\mu(\text{Mo K}\alpha) = 1.182\text{ mm}^{-1}$	$F(0\ 0\ 0) = 1328$
Crystal size = $0.06 \times 0.06 \times 0.33\text{ mm}^3$	
No. of reflections collected = 8535	
No. of independent reflections = 3324	
θ range for data collection: 1.64 to 28.43°	
Data/Restrains/Parameters = 3324/24/181	
Goodness-of-fit on $F^2 = 0.819$	
R indices [$I > 2\sigma(I)$]: $R1 = 0.0356$, $wR2 = 0.0809$	
R indices (all data): $R1 = 0.0921$, $wR2 = 0.0863$	
$(\Delta/\sigma)_{\text{max}} = 0.001$	
$(\Delta\rho)_{\text{max}} = 0.517\text{ e}\text{\AA}^{-3}$	$(\Delta\rho)_{\text{min}} = -0.379\text{ e}\text{\AA}^{-3}$
Measurement: Bruker Smart APEX CCD diffractometer	
Program system: SHELXTL	
Structure determination: Direct methods (SHELXS-97)	
Refinement: full matrix least-squares (SHELXL-97)	
CCDC deposition number: 921025	

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Fig. 2 ORTEP view of the title compound. Crystal water molecules are disordered into four positions with occupancy factors of 0.25. Hydrogen atoms are omitted for clarity. The thermal ellipsoids are shown at the 50% probability level. Symmetry codes: (i) $1/2-x, 3/2-y, -z$; (ii) $1-x, 1-y, 1-z$; (iii) $1-z, y, 3/2-z$.

$C_{20}H_{24}N_2O_8Rh_2 \cdot 0.25H_2O$: C, 38.09; H, 3.92; N, 4.44%. IR (KBr, cm^{-1}): 3056 (ν_{CH}), 1588 (ν_{asCOO}), 1429 (ν_{sCOO}). Diffuse reflectance spectra: λ_{max} 259, 329, 460sh, 518 ($\pi^*(Rh_2) \rightarrow \sigma^*(Rh_2)$) nm. X-ray quality crystals were grown by the slow diffusion of bpe with rhodium(II) acetate in ethanol.

X-ray diffraction data for these crystals were collected at 293 K on a Bruker CCD X-ray diffractometer (SMART APEX) using graphite-monochromated Mo- $K\alpha$ radiation. Crystal data and details concerning data collection are given in Table 1. The structure was solved by direct methods and refined by full-matrix least-squares methods. Crystal water molecules were disordered into four positions with occupancy factors of 0.25. The hydrogen atoms, except for water molecules, were inserted at their calculated positions and fixed there. All of the calculations were carried out on a Pentium IV Windows 2000 computer utilizing the SHELXTL software package.

The molecular structure drawn by ORTEP is shown in Fig. 2. Selected bond distances and angles are given in Table 2S. The crystal structure consists of chain molecules made up of $Rh_2(CH_3CO_2)_4$ and bpe, and water molecules. The asymmetric unit contains one-half of the dinuclear unit and bpe molecule with a crystallographic inversion center at the midpoint of the $Rh(1)-Rh(1)^i$ bond and the center of the bpe moiety, respectively. The $Rh(1)-Rh(1)^i$ distance is $2.3990(8)\text{\AA}$, which is in the range of $2.35 - 2.45\text{\AA}$, found in the majority of dinuclear rhodium(II) carboxylates.⁵⁻⁹ The coordination geometry around the rhodium atom, $Rh(1)$, is a distorted octahedron. One apical position is occupied by the nitrogen atom, $N(1)$, of the bpe molecule. The $Rh(1)$ atom is $0.076\text{\AA}$ above the basal plane formed by $O(1)-O(2)-O(3)-O(4)$ towards the nitrogen atom $N(1)$ of the bpe molecule. The basal bond distances of the Rh and basal O atoms are $2.024(4) - 2.037(4)\text{\AA}$, which are comparable to those found in rhodium(II) acetate and rhodium(II) pivalate and their chain compounds.⁵⁻⁹ The apical $Rh(1)-N(1)$ distance is $2.252(4)\text{\AA}$, which is also in the usual range as apical bonding for the rhodium(II) carboxylate adducts.⁵⁻⁹ The $Rh(1)^i-Rh(1)-N(1)$ angle is $177.53(12)^\circ$, resulting in a zig-zag chain molecule. It is to be noted that the chain molecules are interlinked through the C-H... π interactions to form cavities, as shown in Fig. 3. The crystal structure is similar to that of the corresponding copper(II) species, $[Cu_2(CH_3CO_2)_4(bpe)]_n \cdot$

Fig. 3 Packing diagram of the title compound viewed along the c axis.

$2nH_2O$.¹⁰ In the crystal, water molecules are incorporated in the cavities among the chain molecules. Therefore, we expected the adsorption property to exist for the present compound, and measured the adsorption isotherm of N_2 (77 K). The adsorption isotherm belonged to Type II in IUPAC classification ($S_{BET} = 65.6\text{ m}^2\text{ g}^{-1}$). The sample possessed no micropores, judging from the t -plot analysis (Fig. 5S),⁹ while the pore size distribution curve estimated from the Dollimore-Heal method⁹ showed that this mainly has a mesopore with a mean diameter of ca. 33 nm (Fig. 6S).

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