Synthesis and Crystal Structure of a Chain Complex of Molybdenum(II) Benzoate and 1,2-Bis(4-pyridyl)ethane with an N₂-Adsorption Property

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The title compound, a chain adduct of molybdenum(II) benzoate with 1,2-bis(4-pyridyl)ethane (bpe), catena(tetrakis(μ -benzoato-*O,O'*)(μ -1,2-bis(4-pyridyl)ethane-*N,N'*)dimolybdenum(II)), [Mo₂(C₆H₅CO₂)₄(bpe)]_n, was synthesized; the crystal structure was determined by the single-crystal X-ray diffraction method at 293 K. It crystallizes in the triclinic space group *P* $\bar{1}$ with *a* = 8.2457(17) Å, *b* = 10.506(2) Å, *c* = 12.142(3) Å, α = 114.583(4)°, β = 90.398(4)°, γ = 108.768(4)°, *V* = 893.4(3) Å³, *D*_x = 1.599 g/cm³, *D*_m = 1.60 g/cm³, and *Z* = 1. The *R*1 [*I* > 2σ(*I*)] and *wR*2 (all data) values are 0.0362 and 0.0716, respectively, for all 3971 independent reflections. The molecule has a chain structure with an alternating arrangement of Mo₂(C₆H₅CO₂)₄ and bpe [Mo–Mo 2.1095(5) Å, Mo–N 2.608(2) Å]. The N₂ adsorption isotherm was investigated and a Type II adsorption property with a *S*_{BET} value of 2.47 m² g^{−1} was found.

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We have engaged in a study on polymer compounds based on metal carboxylates with a lantern-like dinuclear structure, because they have unique properties, such as a gas-occlusion behavior.^{1–8} Recently, we reported on the crystal structure of a chain compound of molybdenum(II) benzoate with 4,4'-bipyridyl (4,4'-bpy).⁹ This compound showed a limited adsorption property for N₂ molecules.⁹ In this study, we prepared a chain compound of molybdenum(II) benzoate with 1,2-bis(4-pyridyl)ethane (bpe) in order to examine the crystal structure and the adsorption property by modifying the linking ligand 4,4'-bpy to bpe. The crystal structure of catena(tetrakis(μ -benzoato-*O,O'*)(μ -1,2-bis(4-pyridyl)ethane-*N,N'*)dimolybdenum(II)), [Mo₂(C₆H₅CO₂)₄(bpe)]_n, was determined by X-ray crystallography, and the adsorption

property was studied for N₂, which is the first example of a bpe adduct of molybdenum(II) benzoate, as shown in Fig. 1.

Molybdenum(II) benzoate was prepared by a method described in the literature.¹⁰ A 0.262 g (1.42 mmol) portion of bpe was added to a solution of molybdenum(II) benzoate (0.102

Fig. 1 Chemical structure of the title compound.

Table 1 Crystal and experimental data

Chemical formula: C ₄₀ H ₃₂ Mo ₂ N ₂ O ₈	
Formula weight = 860.56	
<i>T</i> = 293 K	
Crystal system: triclinic	Space group: <i>P</i> $\bar{1}$
<i>a</i> = 8.2457(17) Å	α = 114.583(4)°
<i>b</i> = 10.506(2) Å	β = 90.398(4)°
<i>c</i> = 12.142(3) Å	γ = 108.768(4)°
<i>V</i> = 893.4(3) Å ³	<i>Z</i> = 1
<i>D</i> _x = 1.599 g/cm ³	<i>D</i> _m (floatation) = 1.60 g/cm ³
Radiation: Mo <i>K</i> α (λ = 0.71073 Å)	
μ (Mo <i>K</i> α) = 0.759 mm ^{−1}	<i>F</i> (0 0 0) = 434
Crystal size = 0.25 × 0.15 × 0.08 mm ³	
No. of reflections collected = 5589	
No. of independent reflections = 3971	
θ range for data collection: 1.87 to 28.55°	
Data/Restraints/Parameters = 3971/0/245	
Goodness-of-fit on <i>F</i> ² = 0.896	
<i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)] : <i>R</i> 1 = 0.0362, <i>wR</i> 2 = 0.0689	
<i>R</i> indices (all data): <i>R</i> 1 = 0.0474, <i>wR</i> 2 = 0.0716	
(Δσ) _{max} = 0.001	
(Δρ) _{max} = 0.618 e Å ^{−3}	(Δρ) _{min} = −0.282 e Å ^{−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: 988817	

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Fig. 2 ORTEP view of the title compound. Hydrogen atoms are omitted for clarity. The thermal ellipsoids are shown at the 50% probability level. The carbon atom C(20) of dpe was disordered into two positions, C(20A) and C(20B), with occupation factors of 0.62 and 0.38, respectively. Symmetry codes: (i) $-x, -y, -z$; (ii) $1-x, -1-y, -1-z$.

g, 0.151 mmol) in 10 cm³ of THF-hexane (1:1) under Ar, and the solution was stirred for 24 hrs. The orange precipitate was collected, washed by THF-hexane, and dried under a vacuum. Yield, 0.086 g (66%). *Anal.* Found: C, 55.66; H, 3.41; N, 3.34%. Calcd for C₄₀H₃₂Mo₂N₂O₈: C, 55.83; H, 3.75; N, 3.26%. IR (KBr, cm⁻¹): 3054 (νCH(benzoate)), 1602 (νCN(bpe)), 1508 (ν_{as}COO), 1395 (ν_sCOO). Diffuse reflectance spectra: λ_{max} 226, 264, 418, 488sh (δ(Mo₂)→δ*(Mo₂))nm. X-ray quality crystals were grown by the slow diffusion of bpe in THF-hexane (1:1) with molybdenum(II) benzoate in THF.

X-ray diffraction data for one of these crystals were collected at 293 K on a Bruker CCD X-ray diffractometer (SMART APEX) using graphite-monochromated Mo- K_{α} radiation. Crystal data and details concerning the data collection are given in Table 1. The structure was solved by direct methods, and refined by full-matrix least-squares methods. The carbon atom C(20) of dpe was found to be disordered into two positions, C(20A) and C(20B), with occupation factors of 0.62 and 0.38, respectively. Hydrogen atoms were inserted at their calculated positions, and were included in least-squares calculations using a riding-atom model. All of the calculations were carried out on a Pentium IV Windows 2000 computer utilizing the SHELXTL software package. Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposit number CCDC-988817. Copies of the data can be obtained free of charge *via* <http://www.ccdc.cam.ac.uk/conts/retrieving.html> (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

The structure of the chain molecule 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 by an alternating arrangement of $\text{Mo}_2(\text{C}_6\text{H}_5\text{CO}_2)_4$ and bpe molecules. The asymmetric unit contains one-half of the dinuclear unit and the bpe molecule with a crystallographic inversion center at the midpoint of the Mo(1)–Mo(1)ⁱ bond and the center of the bpe moiety, respectively. The Mo(1)–Mo(1)ⁱ distance is 2.1095(5) Å, which is in the range of 2.06 – 2.15 Å, found in the majority of dinuclear molybdenum(II)

carboxylates.^{4,6-9} The coordination geometries around the Mo(1) atom involves a distorted octahedron. One apical position for the Mo(1) atom is occupied by the N(1) atom of the bpe molecule. The Mo(1) atom is located 0.057(1) Å below basal plane formed by O(1)–O(2)–O(3)–O(4) towards the molybdenum atom Mo(1)ⁱ. This suggests strong metal-metal bonding in the dinuclear molybdenum(II) benzoate core. The basal bond distances of the Mo and basal O atoms [2.0943(19) – 2.1211(19) Å] are comparable to those found in the chain compound of molybdenum(II) benzoate, [Mo₂(C₆H₅CO₂)₄(4,4'-bpy)]_n [2.101(2) – 2.119(2) Å],⁹ whereas the apical Mo(1)–N(1) distance [2.608(2) Å] is a little shorter than the apical Mo–N distances [2.663(3) and 2.647(3) Å] for the chain compounds of molybdenum(II) benzoate.⁹ The Mo(1)ⁱ–Mo(1)–N(1) angle is 168.89(6), which is also comparable to those of [Mo₂(C₆H₅CO₂)₄(4,4'-bpy)]_n, (Mo–Mo–N 167.39(9)[°] and 164.69(8)[°]),⁹ resulting in a zigzag chain molecule. In the crystal, there are no cavities (Fig. 3S). We measured the adsorption isotherm of N₂ (77 K) for the present compound (Fig. 4S). The adsorption isotherm showed that the present compound has a similar adsorbing property with type II in the IUPAC classification for N₂ gas, having a specific surface area, *S*_{BET}, value (2.47 m² g^{−1}) comparable to that of [Mo₂(C₆H₅CO₂)₄(4,4'-bpy)]_n (*S*_{BET} = 2.71 m² g^{−1}),⁹ in accordance with the fact that these crystals possess almost no porous structure.

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