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Article

An Infinite Zigzag Chain of Alternating Cl–Pd–Pd–Cl and Mo–Mo Units

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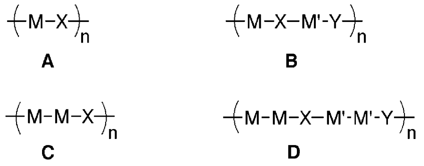
Treatment of $Pd_2Cl_2(CNC_6H_3Me_2\text{-}2,6)_4$ (**1**) with $Mo_2(O_2CCF_3)_4$ (**2**) in dichloromethane afforded an infinite zigzag chain $\{[Pd_2Cl_2(CNC_6H_3Me_2\text{-}2,6)_4][Mo_2(O_2CCF_3)_4]\}_n$ (**3**), where two metal–metal bonded dinuclear Pd–Pd and Mo–Mo units were bridged by chloro atoms. The Mo–Mo distance (2.1312(3) Å) of **3** is significantly elongated compared to that of **2** (2.090(4) Å) and lies in the range of that of the quadruple Mo–Mo bonded complexes. Such elongation might be attributed to the axial donation of the chloro atoms of the Pd–Pd unit to the Mo–Mo moiety.

Introduction

Assembled complexes with highly controlled nuclearity and dimensionality have been extensively investigated, and quasi-one-dimensional materials, especially transition-metal linear-chain complexes, have attracted particular interest in view of their novel electronic, magnetic, and optical properties.[1−3] Among them, halogen-bridged transition metal mononuclear complexes **A** and **B** (Scheme 1) have been major targets of chemists and physicists.[4,5] Chain compounds **C** (Scheme 1) of dinuclear transition metal units bridged by halogen atoms such as $[M_2(dta)_4I]_n$ (M = Pt, Ni; dta = dithioacetate) and $\{[Pt_2(pop)_4X]^{4-}\}_n$ (pop = diphosphonate) have been prepared and their physical properties have been elucidated.[6] Additionally, one-dimensional polymer chains, categorized as **C**, containing dinuclear units, especially $M_2(O_2CR)_4$ ones,[7] and bidentate organic bases, acting as bridging donor ligands, such as pyrazine,[8] ethylenediamine,[9] dimethylphosphinoethane,[9] quinone,[10] 4,4′-bipyridine,[11] polycyano anionic,[12] and polynitriles[13] have been prepared. It is noted that a chain compound **D** (Scheme 1) is categorically new, though we and others have been interested in synthesizing heteropolynuclear linear complexes containing Mo_2^{4+}

Scheme 1



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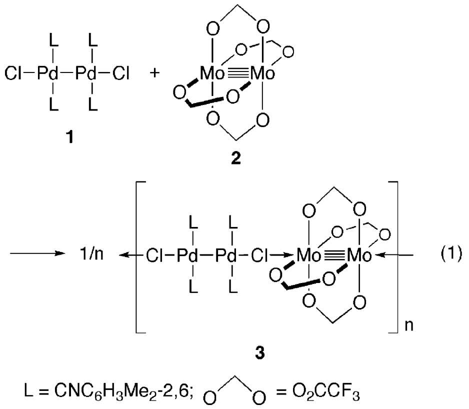
10.1021/ic049397o CCC: $27.50

units and other transition metals such as Pd, Pt, Co, Cu, Fe, or Re in the chains.[14−16]

In this contribution, we report that the chloro atoms bound to the Pd_2^{2+} core of $Pd_2Cl_2(CNC_6H_3Me_2\text{-}2,6)_4$ (**1**) coordinate to the axial positions of $Mo_2(O_2CCF_3)_4$ (**2**) to give a novel infinite polymer chain $\{[Pd_2Cl_2(CNC_6H_3Me_2\text{-}2,6)_4][Mo_2(O_2CCF_3)_4]\}_n$ (**3**) composed of alternating Pd−Pd and Mo−Mo units with bridging chloro atoms [eq 1]. This infinite chain, to the best of our knowledge, is the first example of category **D** where two different metal−metal bonded units are bridged by halogens in the backbone.



Results and Discussion

A solution of **1** in chloroform was mixed with 1 equiv of **2** in chloroform to induce quantitative precipitation of yellow powder of **3**, whose 1:1 formulation was confirmed by combustion analysis and X-ray crystallographic study. The ^1H NMR spectrum of **3** in $CDCl_3$ displayed signals due to **1**, indicating the simple mixture of two starting compounds in solution.

The IR spectrum of **3** indicated a ν(NC) stretch at 2170 cm^{-1}, which is a higher energy by 15 cm^{-1} than that found for **1** (2155 cm^{-1}).[17] A shift to higher energy is typical for isocyanide ligand involving a σ-donation with little metal-to-ligand π-back-bonding. Thus, it is likely that the Pd atoms donate electrons of d-orbitals to the Mo_2 unit through the bridging chloro atoms. For the Mo_2 units in **3**, carbonyl stretching absorption appeared at 1606 cm^{-1}, which is shifted to higher frequency compared with 1592 and 1572 cm^{-1} in **2**.[18] Such a shift has been observed for the axial coordination of donor molecules such as pyridine,[19] 2,2′-bipyridine,[20] methyldiphenylphosphine,[21] ethylenediamine,[22] 1,2-bis(dimethylphosphino)ethane,[9] tetramethylethylenediamine,[9] and quinones.[10] Furthermore, the Raman spectrum of **3** afforded direct information for the Mo−Mo bonding. The Mo−Mo vibration frequency of **3** (powder sample) appeared at 374 cm^{-1}, indicating the significant interaction between the chloro atom bound to the palladium atom and the molybdenum atom since the Mo−Mo stretching frequencies of the starting compound **2**[23] and its axial chloro coordinated compound, $[Et_4N][Mo_2(O_2CCF_3)_4Cl]$,[23] were observed at 398 and 373 cm^{-1}, respectively.

Recrystallization of **3** from hot chloroform afforded orange crystals suitable for X-ray analysis. Figure 1 shows the ORTEP view of each unit of **3**, and the infinite zigzag structure is shown in Figure 2. Two metal−metal bonded dinuclear Pd−Pd and Mo−Mo units, which are bridged by a chloro atom, are alternately arranged with the obtuse angle (123.76(2)°) of Pd−Cl(1)−Mo. It is noteworthy that the Pd−Pd distance (2.5178(3) Å) and the Pd−Cl distance (2.4079(5) Å) are almost the same as those in Pd_2Cl_2(*tert*-BuNC$)_4$ (Pd−Pd = 2.532(2) Å and Pd−Cl = 2.403(9) and 2.416(9) Å),[17]

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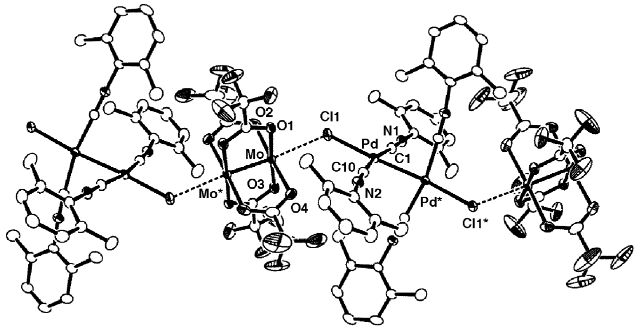

Figure 1. ORTEP view of the unit of the infinite polymer **3** showing the 50% probability thermal ellipsoids. Chloroform as solvate molecules and all hydrogen atoms were omitted for clarity. Selected bond lengths [Å] and angles [deg]: Pd−Pd* 2.5178(3), Mo−Mo* 2.1312(3), Pd−Cl(1) 2.4079(5), Pd−C(1) 1.9524(19), Pd−C(10) 1.9704(19), Mo−Cl(1) 2.7747(5), Mo−O(1) 2.1333(14), Mo−O(2) 2.1193(16); Cl(1)−Pd−Pd* 174.937(14), Cl(1)−Mo−Mo* 174.180(16), Pd−Cl(1)−Mo 123.76(2), Pd*−Pd−Cl(1)−Mo 156.17(13), Mo*−Mo−Cl(1)−Pd 110.32(15).

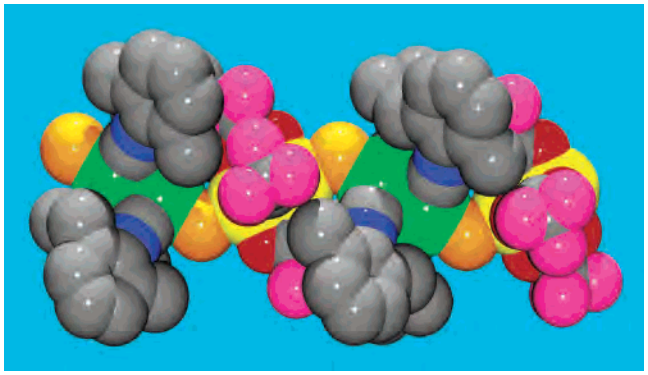

Figure 2. Structure of the infinite zigzag chain of **3**: Mo, yellow; Pd, green; Cl, orange; F, purple; O, red; N, blue; C, gray.

indicating no obvious change in the Cl−Pd−Pd−Cl unit. In sharp contrast, the Mo−Mo distance (2.1312(3) Å) of **3**, the value which lies in the range expected for the quadruple Mo−Mo bond,[2] is significantly elongated compared with that of $Mo_2(O_2CCF_3)_4$ (2.090(4) Å),[18] presumably due to the axial coordination of the chloro atom bound to the palladium atom to the Mo_2 core despite the long Mo−Cl distance of 2.7747(5) Å. Although infinite chain structures of transition metals with chloro atoms as bridges have been reported,[24] to the best of our knowledge **3** is the first example of the infinite chain structure composed of two kinds of dinuclear metal−metal bonded units in its one-dimensional skeleton.

Mass spectrum (ESI) afforded a peak corresponding to the parent ion $\{[Pd_2Cl_2(CNC_6H_3Me_2\text{-}2,6)_4][Mo_2(O_2CCF_3)_4]\}^+$ (m/z = 1452), whereas peaks due to the two discrete precursors were not observed, indicating an associative interaction between the chloro ligand bound to the palladium atom and the Mo_2 moiety.

In summary, we prepared an infinite zigzag chain compound, **3**, as the first example of one-dimensional chains of two dinuclear moieties in its skeleton, i.e., Cl−Pd−Pd−Cl and Mo−Mo units. The elongation of Mo−Mo distance of **3** in solid state compared to that of the precursor **2** was a result of the axial donation of chloro atoms of the Cl−Pd−Pd−Cl unit to the Mo_2 moiety. Further investigations to extend such assembling of discrete dinuclear complexes, as well as characterization of physical properties, are in progress.

Experimental Section

General Procedures. All manipulations involving air- and moisture-sensitive organometallic compounds were carried out using standard Schlenk techniques under argon. Complexes **1**[25] and **2**[18] were prepared according to the literature procedures.

Physical Measurements. Nuclear magnetic resonance (^{1}H NMR) spectra were measured on a Varian-Mercury 300 spectrometer. IR and mass spectra were recorded on a Jasco FT/IR-230 spectrometer, and ESI techniques were performed on a PE-Sciex API-III plus spectrometer. UV−Vis spectra were recorded on an HP 8453 UV−Visible ChemStation using acetonitrile solution in a sealed cell. TGA was measured on a Seiko TG/DTA 6200. Elemental analyses were performed on a Perkin-Elmer 2400 microanalyzer in the Department of Chemistry, Faculty of Engineering Science, Osaka University. Melting point was measured in sealed tubes and was not corrected.

Preparation of 3. A solution of **1** (87.3 mg, 0.108 mmol) in chloroform (10 mL) was added to a solution of **2** (69.4 mg, 0.108 mmol) in chloroform (10 mL) via syringe. The yellow reaction mixture was stirred for 3 h at room temperature. The resulting yellow precipitations were isolated by removal of the supernatant and dried in argon atmosphere, giving **3** as yellow solids (130.3 mg, 83%); mp 211−216 °C (decomp.). The TGA measurement of **3** afforded a peak of weight loss around 30−80 °C due to the release of chloroform before its decomposition temperature. ^{1}H NMR (300 MHz, $CDCl_3$, 35 °C): δ 2.48 (s, 24H, CH_3), 7.09−7.23 (m, 12H, C_6H_3). Raman (solid, cm^{-1}): 374. IR (KBr, cm^{-1}): 2168 (s, ν(NC)), 1684 (w), 1606 (s), 1474 (m), 1194 (s), 1161 (s, ν(CF)), 856 (m), 779 (m), 731 (s), 656 (w), 498 (m), 422 (w). UV (CH_3CN): λ_{max} 262 ($\epsilon = 7.0 \times 10^3$), 313 ($\epsilon = 2.6 \times 10^3$), 491 ($\epsilon$ = 60). ESI-MS: m/z = 1452 (1), 773 (100, base peak), 904 (78), 683 (9). Anal. Calcd for $C_{46}H_{38}Cl_8F_{12}Mo_2N_4O_8Pd_2$: C, 32.67; H, 2.26; N, 3.31. Found: C, 32.65; H, 2.34; N, 3.40.

Crystallographic Data Collections and Structure Determination. Crystals of **3** suitable for X-ray crystallography were grown by cooling its hot solution in chloroform. Orange crystals of **3** suitable for X-ray diffraction study were mounted on the end of a glass fiber with a layer of light mineral oil and placed in a nitrogen stream at 110(1) K. Data for **3** were collected by a Rigaku RAXIS-RAPID equipped with a sealed-tube X-ray generator (50 kV, 40 mA) with monochromatized Mo−Kα (0.71075 Å) radiation in a nitrogen stream at 110(1) K. Indexing was performed from 3 oscillations which were exposed for 90 s. The unit cell parameters and the orientation matrix for data collection were determined by the least-squares refinement with the setting angles listed in Table 1. A symmetry-related absorption was corrected by use of the program ABSCOR[26a] with transmission factors. Details of the data collection are summarized in Table 1.

Structure Determination and Refinement. The structure of **3** was solved by direct methods (SIR-97)[26b] and refined on F^2 by

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Table 1. Crystallographic Data of and Structure Refinement for **3**·2CHCl$_3$^{a,b}

empirical formula	$C_{46}H_{38}Cl_8F_{12}Mo_2N_4O_8Pd_2$
fw	1691.08
temp, K	110(1)
wavelength, Å	0.71075
cryst syst, space group	monoclinic, $C2/c$
a, Å	14.5231(2)
b, Å	15.7412(3)
c, Å	26.7104(4)
β, deg	96.329(1)
vol, Å^3	6069.08(17)
Z	4
calculated density, g/cm^3	1.851
abs coeff	1.427
F(000)	3304
crystal size, mm	0.50 × 0.30 × 0.20
θ range for data collection, deg	3.01 to 32.58
limiting indices	$-21 \le h \le 21$, $-23 \le k \le 23$, $-40 \le l \le 40$
reflns collected/unique	127288/11039 [R(int) = 0.0312]
completeness to $\theta = 32.58$	99.9%
max. and min. transmission	0.8793 and 0.7110
data/restraints/parameters	11039/13/461
GOF on F^2	1.045
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0311$, $wR_2 = 0.0748$
R indices (all data)	$R_1 = 0.0372$, $wR_2 = 0.0770$
largest diff. peak and hole, e/Å^3	0.901 and −0.821

^{a} $R_1 = (\sum||F_o| - |F_c||)/\sum|F_o|$. ^{b} $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum(wF_o^4)]^{1/2}$.

full-matrix least-squares methods, using SHELXL-97.[26c] All non-hydrogen atoms except Cl atoms of solvate chloroform were anisotropically refined. A molecule of solvate chloroform was located in the asymmetric unit. The three chlorine atoms of the solvate chloroform were disordered and 18 sites were found on a difference Fourier map. The sum of the site occupancy factors of Cl atoms was 2.98951. The C−Cl bonds of chloroform were restrained to 1.772(20) Å in the refinements. Hydrogen atoms of methyl groups were included in the refinement on calculated positions riding on their carrier atoms (Csp^3-H = 0.98 Å, Uiso(H) = 1.5*Ueq(C) Å^2) and the other hydrogen atoms were isotropically refined. All calculations of least-squares refinements were performed with SHELXL-97 programs on the Origin 3400 computer of Silicon Graphics Inc. at the Research Center for Structural Biology Institute for Protein Research, Osaka University. Details are summarized in the Supporting Information. An X-ray crystallographic file in CIF format has been deposited at the Cambridge Data Center and is available as Supporting Information.

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Supporting Information Available: X-ray crystallographic file for **3**, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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