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Synthesis and characterization of tricarbonyl–molybdenum complexes bearing monoaza-trithia-macrocyclic ligands



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1. Introduction

Sulfur-containing macrocyclic compounds such as thia-, oxathia-, and azathiacrown ethers show high affinity to transition metals with various oxidation states (especially group 6 metals) forming stable complexes with them [1-5]. Therefore, a lot of studies were performed to develop various reagent and catalyst using a metal complex bearing macrocyclic ligand [6-8]. And, it is known that metal-carbonyl complexes are very useful tool for investigating the property of metal complex such as a structure and electronic state. Carbon monoxide can bind strongly to low oxidation state transition metals. And, it shows distinctive peaks that can be an indicator of property of metal complexes in vibration spectroscopy [9–11]. And, conversion of CO molecule is very important process in C1 chemistry. Especially, molybdenum-carbonyl complexes are getting a lot more attention lately. Because it has been reported that vanadium/molybdenum nitrogenases catalyze reductive catenation of carbon monoxide to ethylene, ethane, propylene, propane and so on [12–14].

Thus, we synthesized two types of macrocyclic ligands, 1,4,7trithia-10-azacyclododecane [15] and 1,4,7-trithia-11-azacyclotetradecane [16,17] to provide coordination sphere which can coordinate to low oxidation state molybdenum ion, and prepared molybdenum carbonyl complexes with these ligands. In addition, we investigated the properties of these molybdenum complexes using X-ray diffraction analysis and vibration spectroscopic studies.

ABSTRACT

Novel tricarbonyl–molybdenum complexes bearing monoaza-trithia-macrocyclic ligands (LX^R) , $[Mo(CO)_3(LX^R)]$ (X = 12 or 14, R = H), and $[Mo(CO)_3(L14^{Py})Mo(CO)_4]$ have been synthesized to gain an understanding of the unique properties of macrocyclic ligands. X-ray structure analysis of $[Mo(CO)_3(L14^H)]$ has revealed that intra- and intermolecular hydrogen bonds existed and these interaction regulated CO bond lengths. In addition, vibrational spectroscopy indicates that a specific hydrogen bonding interaction affects the strength of the binding of carbon monoxide molecules to the metal. In case of using $L14^{Py}$, it is expected that dinuclear molybdenum complex was generated.

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Interestingly, we found that the coordination structures of these molybdenum complexes and the coordinated carbonyl molecules are affected by the hydrogen bonds formed in the crystal.

2. Experimental

2.1. Material and methods

All manipulations were carried out under atmospheric conditions of purified argon or dinitrogen gas in an mBRAUN MB 150B-G glovebox or by standard Schlenk techniques. ¹H NMR (300 MHz: Varian, 600 MHz: Bruker) and ¹³C{¹H} NMR (75 MHz: Varian, 150 MHz: Bruker) spectra were measured on a Varian Mercury 300 spectrometer or a Bruker Avance 600 spectrometer, and ¹H and ¹³C{¹H} chemical shifts were estimated relative to an internal standard of tetramethylsilane (TMS) or residual protons in the deuterated solvent. Fourier transform infrared (FT-IR) spectra of solid compounds were obtained from KBr pellets using a JASCO FT/IR-410 spectrophotometer. Electrospray ionization time-offlight mass spectra ESI-TOF/MS were obtained with a Micromass LCT spectrometer. Elemental analyses were obtained with a Perkin Elmer CHN-900 elemental analyzer. Energy dispersive X-ray fluorescence analyses (EDX) were performed by EDX-800, Shimadzu Co. Ltd. The reagents and solvents employed were commercially available. All anhydrous solvents were purchased from Wako Ltd or Sigma-Aldrich, and were degassed with argon or dinitrogen. Molecular mechanics calculations were performed by Fujitsu CACHE program.



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2.2. X-ray crystallography

Single crystals of **1**^{Py} and **2**^H suitable for X-ray diffraction analyses were obtained from CH₂Cl₂/Et₂O solutions after standing for a few days under a N₂ atmosphere. A crystal was mounted on a glass fiber, and diffraction data were collected on a Rigaku/MSC Mercury CCD using graphite monochromated Mo K α radiation at 173 K. The structures were solved by a combination of direct methods (SIR 92 or shelx97) and Fourier techniques. All nonhydrogen atoms except for some of the solvent molecules were refined anisotropically. Hydrogen atoms were refined using the riding model. A Sheldrick weighting scheme was employed. Plots of $\Sigma w(|F_0| - |F_c|)^2$ versus $|F_0|$, reflection order in data collection, $\sin \theta / \lambda$, and various classes of indices showed no unusual tendencies. Neutral atomic scattering factors were obtained from the International Tables for X-ray Crystallography Vol. IV [18]. Anomalous dispersion terms were included in F_{calc} [19] and the values for $\Delta f'$ and $\Delta f''$ were taken from International Tables for X-ray Crystallography Vol. C [20]. The values for the mass attenuation coefficients were obtained from International Tables for X-ray Crystallography Vol. C [21]. All calculations were performed using the crystallographic software package CRYSTALSTRUCTURE [22,23]. A summary of crystallographic data is provided in the supporting information (Table 1).

2.3. Synthesis

2.3.1. N-(2-pyridylmethyl)-1,4,7-trithia-10-azacyclododecane (L12^{Py})

Under an argon atmosphere, a solution of 1,4,7-trithia-10-azacyclododecane (0.350 g, 1.57 mmol), 2-(chloromethyl)pyridine hydrochloride (0.257 g, 1.58 mmol), and triethylamine (0.406 g, 4.02 mmol) in ethanol (50 mL) was refluxed at 75 °C for 30 h. The solvent was removed in vacuo, and then the residue was dissolved in CHCl₃ (200 mL) and washed liberally with water. The organic fraction was dried by MgSO₄, and the solvent was removed to obtain a yellow solid. The residue was purified by column chromatography on silica gel using a mixture of CH₂Cl₂/AcOEt (7:3 v/v ratio) as eluent. Yield 0.320 g, 1.02 mmol (yield 65.0%).

¹H NMR (δ /ppm from TMS in CDCl₃, 600 MHz): δ 2.68 (t, 4H, NCH₂CH₂), 2.83 (m, 12H, NCH₂CH₂SCH₂CH₂S), 3.81 (s, 2H,

Table 1

Summary of crystallographic data.

Complex	1 ^{Py}	2 ^H
Formula	C17H22MoN2O3S3	C ₂₆ H ₄₂ Mo ₂ N ₂ O ₆ S ₆
Formula weight	494.49	862.87
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/c$ (#14)	Pna2 ₁ (#33)
a (Å)	19.1121(8)	29.541(4)
b (Å)	8.2591(3)	8.9741(11)
c (Å)	12.8459(5)	12.783(2)
α (°)	90	90
β (°)	104.630(3)	90
γ (°)	90	90
$V(Å^3)$	1962.0(2)	3388.8(8)
Ζ	4	4
D_{calc} (g cm ⁻³)	1.674	1.691
μ (Mo K α) (cm ⁻¹)	10.063	11.496
Reflection/parameter ratio	19.12	19.38
Reflection collected	14850	25693
Independent reflections (R_{int})	4494 (0.0161)	7676 (0.0339)
Observed reflections ^a	4494	12126
R_1^{a}	0.0239	0.0337
wR_2^a	0.0551	0.0665
Goodness-of-fit (GOF)	1.090	1.098
Largest difference in peak and hole $(e \text{ Å}^{-3})$	0.67, -0.41	0.84, -0.72

^a All reflections.

NCH₂-pyridine), 7.18, 7.50, 7.68, 8.53 (m, 4H, pyridine). ${}^{13}C{}^{1}H$ } NMR (δ /ppm vs TMS in CDCl₃, 150 MHz): δ 26.0 (SCH₂CH₂N), 28.0, 28.8 (SCH₂CH₂S), 52.0 (SCH₂CH₂N), 60.8 (NCH₂-pyridine), 122.3, 122.9, 136.5, 149.1, 159.0 (pyridine).

FT-IR (KBr, cm⁻¹) 3049, 3006, 2961, 2933, 2841, 1588, 1569, 1472, 1453, 1426, 1260, 800.

ESI-TOF-MS (pos.) $m/z = 315.0 [M+H]^+$.

Anal. Calc. for C₁₄H₂₂N₂S₃: C, 53.46; H, 7.05; N, 8.91. Found: C, 52.94; H, 7.26; N, 8.62%.

2.3.2. N-(2-pyridylmethyl)-1,4,7-trithia-11-azacyclotetradecane (L14^{Py})

This compound was prepared by a modification of a literature procedure [6,15–17]. The treatment of 1,4,7-trithia-11-azacyclote-tradecane (0.350 g, 1.57 mmol) and 2-(chloromethyl)pyridine hydrochloride (0.257 g, 1.58 mmol) afforded the objective product (0.320 g, 1.02 mmol) with a 64.9% yield as a solid after chromatography on silica gel (CH₂Cl₂/AcOEt 10: 1 eluent) and drying under reduced pressure.

¹H NMR (δ/ppm from TMS in CDCl₃, 300 MHz): δ 1.79 (q, 4H, NCH₂CH₂CH₂N), 2.59 (m, 8H, NCH₂CH₂CH₂N), 2.78 (m, 8H, SCH₂-CH₂S), 3.72 (s, 2H, NCH₂-pyridine), 7.17, 7.42, 7.70, 8.53 (s m, 4H, pyridine). ¹³C{¹H} NMR (δ/ppm from TMS in CDCl₃, 150 MHz): δ 27.9 (SCH₂CH₂CH₂N), 29.5 (SCH₂CH₂CH₂N), 31.0, 31.4 (SCH₂CH₂S), 53.0 (SCH₂CH₂CH₂N), 61.9 (NCH₂-pyridine), 122.0, 123.0, 136.3, 149.0, 159.8 (pyridine).

FT-IR (KBr, cm⁻¹) 3046, 3010, 2946, 2931, 2798, 1587, 1570, 1469, 1431, 1274, 761.

ESI-TOF-MS (pos.) $m/z = 343.06 [M+H]^+$.

2.3.3. [Mo(CO)₃(L12^H)] (1^H)

A suspension of $L12^{H}$ (1.03 × 10⁻¹ g, 3.26 × 10⁻⁴ mol) and molybdenum hexacarbonyl [Mo(CO)₆] (1.12 × 10⁻¹ g, 4.24 × 10⁻⁴ mol) in toluene (5 mL) was refluxed overnight. The reaction mixture was concentrated in vacuo. The resulting brown solid was dissolved in CH₂Cl₂ (5 mL) and was filtered through a Celite pad. Crystallization from CH₂Cl₂/Et₂O yielded brown crystals of 1^H.

¹H NMR (δ/ppm from TMS in CD₃CN, 300 MHz): δ 2.15 (s, 2H), 2.64 (t, 2H), 2.73 (br, 3H), 2.83 (m, 5H), 2.98 (br, 2H), 3.10 (br, 3H).

FT-IR (KBr, cm⁻¹) δ 3258 (N–H), 1913, 1781, 1754 (C \equiv O), 517, 473 (Mo–C).

ESI-TOF-MS (pos.) $m/z = 377.9 [M-CO]^+$.

Anal. Calc. for C₁₁H₁₇MoNO₃S₃: C, 32.75; H, 4.25; N, 3.47. Found: C, 32.56; H, 4.48; N, 3.29%.

2.3.4. fac-[Mo(CO)₃(L12^{py})] (1^{py})

According to a procedure similar to the procedure used for preparation of $\mathbf{1}^{H}$, a suspension of $\mathbf{L12}^{Py}$ (1.23×10^{-1} g, 3.91×10^{-4} mol) and molybdenum hexacarbonyl [Mo(CO)₆] (1.23×10^{-1} g, (4.66×10^{-4} mol) in toluene (5 mL) was refluxed for 8 h. The reaction mixture was concentrated in vacuo, and then the resulting brown solid was dissolved in CH₂Cl₂ (5 mL) and filtered through a Celite pad. Crystallization from CH₂Cl₂/*n*-pentane yielded yellow crystals of $\mathbf{1}^{Py}$.

¹H NMR (δ /ppm from TMS in CDCl₃, 300 MHz): δ 2.6–3.2 (m, 16H, macrocycle), 4.04 (s, 2H, NCH₂Py), 7.37 (d, 1H, pyridine-3H), 7.71, 7.80 (t, 1H, pyridine-4,5H), 8.91 (d, 1H, pyridine-6H).

 $^{13}C\{^{1}H\}$ NMR (δ /ppm from CDCl₃ in CDCl₃, 75 MHz) δ 24.09, 27.75, 28.90, 57.04, 65.21, 123.09, 123.92, 138.04, 153.32, 217.55, 221.95, 231.34.

FT-IR (KBr, cm⁻¹) δ 1901, 1763 (C=0), 515, 462 (Mo-C).

Anal. Calc. for $C_{17}H_{22}MoN_2O_3S_3$: C, 41.29; H, 4.48; N, 5.66. Found: C, 41.74; H, 4.85; N, 5.66%.

2.3.5. *fac-[Mo(CO)₃(L14^H)]* (2^H)

According to a procedure similar to the procedure used for preparation of 1^{H} , a suspension of $L14^{\text{H}}$ (1.39×10^{-1} g, 5.54×10^{-4} mol) and molybdenum hexacarbonyl [Mo(CO)₆] (1.50×10^{-1} g, 5.69×10^{-4} mol) in toluene (5 mL) was refluxed for 8 h. The reaction mixture was concentrated in vacuo, and then the resulting brown solid was dissolved in CH₂Cl₂ (5 mL) and filtered through a Celite pad. Crystallization from CH₂Cl₂/*n*-hexane yielded yellow crystals of 2^{H} .

¹H NMR (δ /ppm from TMS in CDCl₃, 600 MHz) δ 1.90 (br, 2H), 2.18 (m, 2H), 2.34 (m, 2H), 2.60 (m, 2H), 2.70 (m, 4H), 2.81 (s, 1H), 2.90 (m, 2H), 3.19 (br, 4H), 3.25 (m, 2H).

 $^{13}C\{^{1}H\}$ NMR (δ/ppm from CDCl₃ in CDCl₃, 150 MHz) d 27.70, 34.66, 35.07, 38.36, 47.12, 221.12 (CO), 223.78 (CO).

FT-IR (KBr, cm⁻¹) δ 3347 (N–H), 1910, 1790 (C=O), 517, 471 (Mo–C).

Anal. Calc. for C₁₃H₂₁MoNO₃S₃: C, 36.19; H, 4.91; N, 3.25. Found: C, 35.99; H, 4.88; N, 3.20%.

2.3.6. $[Mo(CO)_3(L14^{Py})Mo(CO)_4](2^{Py})$

According to a procedure similar to the procedure used for preparation of 1^{H} , a suspension of $L14^{\text{Py}}$ (1.60×10^{-1} g, 4.67×10^{-4} mol) and molybdenum hexacarbonyl [Mo(CO)₆] (1.23×10^{-1} g, 4.66×10^{-4} mol) in toluene (5 mL) was refluxed for 8 h. The reaction mixture was concentrated in vacuo, and then the resulting brown solid was washed with THF and CH₂Cl₂. Dinuclear molybdenum complex [Mo(CO)₃($L14^{\text{Py}}$)Mo(CO)₄] was yielded as pale yellow powder.

FT-IR (KBr, cm⁻¹) δ 2007, 1917, 1871, 1820, 1786 (C=O), 457 (Mo–C).

Anal. Calc. for C₁₃H₂₁MoNO₃S₃: C, 37.81; H, 3.59; N, 3.83. Found: C, 38.20; H, 3.64; N, 3.80%.

3. Results and discussion

Monoaza-trithia-macrocyclic ligands were synthesized according to literature procedures with slight modifications [15–17]. Reactions of 3-thia-1,5-pentanedithiol with bis(2-chloroethyl)amine and bis(2-chloropropyl)amine in the presence of cesium carbonate in DMF gave 1,4,7-trithia-10-monoazacyclododecane ($L12^{H}$) and 1,4,7-trithia-11-monoazacyclotetradecane ($L14^{H}$), respectively. The reactions of LX^H (X = 12 and 14) with 2-(chloromethyl)pyridine in the presence of triethylamine in ethanol gave N-substituted ligands, N-(2-pyridylmethyl)-1,4,7-trithia-10-azacyclododecane ($L12^{Py}$) and N-(2-pyridylmethyl)-1,4,7-trithia-11-azacyclotetradecane ($L14^{Py}$), respectively (Scheme 1). The structures of these ligands were confirmed by several techniques (NMR, FT-IR, and elemental analysis).

Molybdenum tricarbonyl complexes have been synthesized from molybdenum hexacarbonyl and the corresponding macrocycle ligands. Fortunately, in each case of $fac-[(L12^{py})Mo(CO)_3]$ (1^{py})



Scheme 1. Synthesis of L12Py and L14Py.

and fac-[(**L14**^H)Mo(CO)₃] (**2**^H), a single crystal suitable for X-ray structure analysis was obtained. Molecular structures of **1**^{Py} and 2^{H} are shown in Figs. 1 and 2, respectively. The selected interatomic distances and angles for 1^{Py} and 2^{H} are listed in Tables 2 and 3, respectively. The crystal structure of **2^H** revealed that it contains two slightly different independent molecules in the unit cell. For both 1^{Py} and 2^H, each molybdenum center is octahedrally coordinated with three carbon monoxide molecules coordinated to the metal center in a facial fashion. For **1**^{Py}, the remaining three sites are coordinated by one pyridine nitrogen atom, one sulfur atom, and one alkyl amine nitrogen atom of the macrocyclic ligand **L12**^{py}. In contrast, for **2**^H, the metal ion is coordinated by three sul-fur atoms of ligand **L14**^H, and not coordinated by any of the alkyl amine nitrogen atoms. The different coordination arrangements provided by the two ligands can be explained by the chelate effect. For 1^{Py} , the pyridine nitrogen, which is a strong π -acceptor ligand. coordinates to molvbdenum to form a five-membered chelate ring with an alkyl amine nitrogen. In the case of **2^H**, the five-membered chelate ring formed with three sulfur atoms for molybdenum is more stable than the six-membered chelate ring with two sulfur atoms instead of one alkyl amine nitrogen. Interestingly, an intramolecular hydrogen bond was identified in crystal 2^H; $N(1) \cdots S(1) = 3.037 \text{ Å}$ and $N(2) \cdots S(6) = 3.041 \text{ Å}$ [24]. These hydrogen bonds may inhibit the coordination of an alkyl amine nitrogen atom to the molybdenum center. The Mo-CO bonds for 1^{Py} are 1.9410(17) Å for Mo(1)-C(1), 1.9390(19) Å for Mo(1)-C(2), and 1.9381(17) Å for Mo(1)-C(3), respectively. The Mo-S length is 2.5935(5) Å for Mo(1)–S(1), and the Mo(1)–N_{alkvl}(1) and



Fig. 1. Molecular structure of *fac*-[(**L12**^{Py})Mo(CO)₃] (1^{Py}) with 50% thermal ellipsoids. Hydrogen atoms are omitted for clarity.



Fig. 2. Molecular structure of fac-[(**L14**^H)Mo(CO)₃] (**2**^H) with 50% thermal ellipsoids. Hydrogen atoms are omitted for clarity.

Table 2	
Selected interatomic distances and angles of <i>fac</i> -[Mo(CO) ₃ (L12 ^{Py})] (1 ^{Py}).	

Atom distances (Å)			
C(1) - O(1)	1.172(2)	C(2) - O(2)	1.165(3)
C(3) - O(3)	1.164(3)	Mo(1) - C(1)	1.9410(17)
Mo(1)-C(2)	1.9390(19)	Mo(1)-C(3)	1.9381(17)
Mo(1)-S(1)	2.5935(5)	Mo(1)-N(1)	2.3752(13)
Mo(1) - N(2)	2.2689(13)		
$Mo(1) \cdot \cdot \cdot S(2)$	4.8002(5)	$Mo(1) \cdot \cdot \cdot S(3)$	5.2129(4)
Bond angles (Å)			
Mo(1)-C(1)-O(1)	175.94(16)	Mo(1)-C(2)-O(2)	174.71(16)
Mo(1)-C(3)-O(3)	174.44(18)	C(1) - Mo1 - N(2)	177.81(7)
C(2) - Mo(1) - S(1)	173.38(6)	C(3) - Mo(1) - N(1)	166.61(6)
N(1)-Mo(1)-N(2)	73.26(5)	N(1)-Mo(1)-S(1)	79.76(4)
S(1)-Mo(1)-N(2)	75.30(4)		

Table 3

Selected interatomic distances and	angles of fac-[M	$lo(CO)_3(L14^H)] (2^H).$	
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Atom distances (Å)			
AC(1)-O(1)	1.156(5)	C(14)-O(4)	1.179(5)
C(2) - O(2)	1.170(4)	C(15) - O(5)	1.169(5)
C(3)-O(3)	1.150(6)	C(16) - O(6)	1.159(6)
Mo(1)-C(1)	1.948(4)	Mo(2)-C(14)	1.928(4)
Mo(1)-C(2)	1.933(4)	Mo(2)-C(15)	1.939(4)
Mo(1)-C(3)	1.972(4)	Mo(2)-C(16)	1.946(4)
Mo(1)-S(1)	2.5804(10)	Mo(2)-S(4)	2.5830(11)
Mo(1)-S(2)	2.5556(12)	Mo(2)-S(5)	2.5581(9)
Mo(1)-S(3)	2.5597(9)	Mo(2)-S(6)	2.6148(10)
$Mo(1) \cdot \cdot \cdot N(1)$	4.397(5)	$Mo(2) \cdots N(2)$	4.217(5)
Bond angles (°)			
Mo(1)-C(1)-O(1)	175.6(4)	Mo(2)-C(14)-O(4)	173.8(4)
Mo(1)-C(2)-O(2)	177.3(3)	Mo(2)-C(15)-O(5)	175.5(4)
Mo(1)-C(3)-O(3)	177.3(4)	Mo(3)-C(16)-O(6)	176.2(4)
C(1)-Mo1-S(2)	178.38(11)	C(14)-Mo(2)-S(5)	177.54(14)
C(2)-Mo(1)-S(3)	177.05(13)	C(15)-Mo(2)-S(6)	171.69(11)
C(3)-Mo(1)-S(1)	172.72(12)	C(16)-Mo(2)-S(4)	176.96(12)
S1-Mo(1)-S(2)	77.15(4)	S(4) - Mo(2) - S(5)	82.01(4)
S(2)-Mo(1)-S(3)	83.24(4)	S(5)-Mo(2)-S(6)	75.28(3)
S(1)-Mo(1)-S(3)	90.30(4)	S(4)-Mo(2)-S(6)	90.79(4)

Mo(1)–N_{pyridine}(2) bond lengths are 2.3752(13) Å and 2.2689(13) Å, respectively. The Mo–N_{pyridine} bond length is shorter than that of Mo–N_{alkyl}. This can be explained by the strong π -acceptor binding ability of pyridine ligand. For **1**^{Py}, the C–O lengths of carbonyl groups are 1.172(2) Å for C(1)–O(1), 1.165(3) Å for C(2)–O(2), and 1.164(3) Å for C(3)–O(3), respectively. These C=O bond lengths are slightly longer than that of the free carbon monoxide molecule (1.128 Å) [25]. In case of **2**^H, the Mo–CO bond lengths are 1.948(4) Å for Mo(1)–C(1), 1.933(4) Å for Mo(1)–C(2),

Table 4

Comparison of selected bond lengths for triscarbonyl-molybdenum complexes.^a

1.972(4) Å for Mo(1)-C(3), 1.928(4) Å for Mo(2)-C(14), 1.939(4) Å for Mo(2)–C(15), and 1.946(4) Å for Mo(2)–C(16), respectively. The Mo–S bond lengths of 2^{H} are 2.5804(10) Å for Mo(1)–S(1), 2.5556(12) Å for Mo(1)-S(2), 2.5597(9) Å for Mo(1)-S(3), 2.5830(11) Å for Mo(2)-S(4), 2.5581(9) Å for Mo(2)-S(5), and 2.6148(10) Å for Mo(2)-S(6), respectively. Although these sulfur atoms are provided by the same alkylthioether, the Mo(1)-S(1)and Mo(2)–S(6) bond lengths are longer than other Mo–S bonds. This may be explained as the result of the S(1) and S(6) atoms operating as hydrogen bond acceptors with N(1) and N(2), respectively. The C \equiv O bond lengths of **2**^H are 1.156(5) Å for C(1)–O(1), 1.170(4) Å for C(2)–O(2), 1.150(6) Å for C(3)–O(3), 1.179(5) Å for C(14)-O(4), 1.169(5)Å for C(15)-O(5), and 1.159(6)Å for C(16)-O(6), respectively. Unlike the case of 1^{Py} , the C(2)-O(2)and C(14)-O(4) bond lengths for 2^{H} are slightly longer than the C(3)-O(3) and C(15)-O(5) bond lengths. This may be dependent upon the presence or absence of a weak interaction because the former two groups form an intermolecular hydrogen bonding interaction and the latter ones do not have such an interaction; $O2 \cdots N2 = 3.330$ Å and $O4 \cdots N1 = 3.308$ Å. The C(3)-O(3) and C(15)-O(5) bonds that are located at the trans positions of S(1)and S(6) are not elongated, although S(1) and S(6) have the hydrogen bond and Mo(1)-S(1) and Mo(2)-S(6) bond lengths are elongated. These findings indicate that intra- and intermolecular hydrogen bonds play an important role in controlling the reactivity of the molybdenum center and carbon monoxide molecules.

Comparisons of crystal structures of 1^{Py} and 2^{H} with those of several tricarbonyl molybdenum complexes reported previously shows that $C \equiv O$ bond lengths of $fac-[Mo(CO)_3(TACN)]$ (TACN = 1,4,7-trisisopropyl-1,4,7-triazacyclononane) [26] which contain three coordinated alkylamine nitrogen atoms, are longer than those of fac-[Mo(CO)₃(TTCN)] (TTCN = 1,4,7-trithiacyclononane) [27] which contain three coordinated sulfur atoms (Table 4). This result indicates that π -back donation from molybdenum to sulfur atoms reduces the π -back donation from molybdenum to the carbonyl molecule. For **1**^{Py} with various coordinated atoms (alkylamine, alkylthioether, and pyridine nitrogen), the C=O bond lengths are between those of fac-[Mo(CO)₃(TACN)] and fac-[Mo(CO)₃(TTCN)]. The shorter Mo– $N_{pyridine}$ bond relative to the Mo–S or Mo– N_{alkyl} bond lengths in $\mathbf{1}^{Py}$ is similar to the Mo– $N_{pyridine}$ dine bond of fac-[Mo(CO)₃(TPA)] (TPA = tris(2-pyridylmethyl)amine) [28]. The Mo–S and C–O bond lengths of 2^{H} are similar to those of fac-[Mo(CO)₃(TTCN)] except for the Mo complexes with hydrogen bonds.

In order to clarify the contribution of hydrogen bonds, we measured FT-IR spectra of molybdenum tricarbonyl complexes with macrocyclic ligands (Fig. 3). The v(N-H) values of $\mathbf{1}^{H}$ and $\mathbf{2}^{H}$ are

$[Mo(CO)_3L]$						
L	L12 ^{Py}	L14^H (I)	L14^H (II)	TACN ^b	TTCN ^c	TPA ^d
Mo-S or N (Å)	2.5935(5) (S)	2.5804(10) (S)	2.5830(11) (S)	2.360(2) (N)	2.512(6) (S)	2.333(5) (N)
	2.3752(13) (N)	2.5556(12) (S)	2.5581(9) (S)	2.371(2) (N)	2.504(6) (S)	2.253(5) (Py)
	2.2689(13) (Py)	2.5597(9) (S)	2.6148(10) (S)	2.377(2) (N)	2.534(7) (S)	2.255(5) (py)
Mo-C (Å)	1.9410(17)	1.948(4)	1.928(4)	1.914(3)	1.94(2)	1.915(8)
	1.9390(19)	1.933(4)	1.939(4)	1.921(3)	1.97(2)	1.930(7)
	1.9381(17)	1.972(4)	1.946(4)	1.920(3)	1.93(2)	1.950(7)
C–O (Å)	1.172(2)	1.156(5)	1.179(5)	1.190(4)	1.15(2)	-
	1.165(3)	1.170(4)	1.169(5)	1.178(3)	1.15(2)	-
	1.164(3)	1.150(6)	1.159(6)	1.173(4)	1.18(2)	-

^a S = thioether, N = alkylamine, Py = pyridine nitrogen, italic characters = with hydrogen bond.

^b TACN = 1,4,7-tris-isopropyl-1,4,7-triazacyclononane, Ref. [26].

^c TTCN = 1,4,7-trithiacyclononane, Ref. [27].

^d TPA = tris(2-pyridylmethyl)amine, Ref. [28].



Fig. 3. FT-IR spectra of molybdenum-carbonyl complexes (KBr method).

 Table 5

 Solid state IR spectral data of [Mo(CO)₃L] complexes.

[Mo(CO) ₃ L]	v(C≡=0) (cm ⁻¹)
$ \begin{array}{l} 1^{H} (L12^{H}) \\ 1^{Py} (L12^{Py}) \\ 2^{H} (L14^{H}) \\ 2^{Py} (L14^{Py}) \end{array} $	1913(A_1), 1781, 1754(E) 1901(A_1), 1763(E) 1910(A_1), 1790(E) 2007, 1017(A_1), 1871, 1820, 1786(E)
$[Mo(CO)_{3}(TACN)]^{a}$ $[Mo(CO)_{3}(TTCN)]^{b}$ $[Mo(CO)_{3}(TPA)]^{c}$ $[Mo(CO)_{4}(dimine)]^{d}$ $[Mo(CO)_{6}]^{e}$	2007, 1917(A ₁), 1871, 1820, 1786(E) 1892(A ₁), 1741, 1720(E) 1900(A ₁), 1759(E) 1915(A ₁), 1783(E) 2010, 1890, 1870, 1820. 2155(A ₁), 1983(E)

^a TACN = 1,4,7-tris-isopropyl-1,4,7-triazacyclononane, Ref. [26].

^b TTCN = 1,4,7-trithiacyclononane, Ref. [27].

^c TPA = tris(2-pyridylmethyl)amine, Ref. [28].

^d dimine = $CH_3(C_6H_5)C = N(CH_2)_2N = C(C_6H_5)CH_3$, Ref. [29].

e Ref. [31].

3258 and 3347 cm⁻¹, respectively. This large difference suggests that an intramolecular hydrogen bond exists in 2^H, but not in 1^H. This is explained by the effect of the chain length of the ethyl group in **1^H**, which is too short to form the intramolecular hydrogen bond. Next, the $v(C \equiv 0)$ (A₁ mode) values of **1**^R and **2**^R (R = H, Py) are listed in Table 5 together with those of several tricarbonyl molybdenum complexes reported previously. Here, the $v(C \equiv 0)$ values with E mode are not completely assigned because of their overlap with other peaks. The $v(C \equiv 0)$ values of $\mathbf{1}^{R}$ and $\mathbf{2}^{R}$ (R = H, Py) are 1913, 1781 and 1754 cm⁻¹ for 1^H; 1901 and 1763 cm⁻¹ for 1^{Py}; 1910 and 1790 cm⁻¹ for **2^H**; and 2007, 1917, 1871, 1820, and 1786 cm⁻¹ for 2^{Py} . The $v(C \equiv 0)$ values for 2^{Py} are quite different from those of the other three complexes. This suggests that the structure of 2^{Py} is different from the structures of 1^{H} , 1^{Py} and 2^{H} . To further discuss, we tried additional characterizations, but solubility for **2**^{Py} is extremely low for several solvents. It is difficult to characterize it in solution state. However, based on FT-IR and elemental analysis, we assigned 2^{Py} as a dinuclear metal complex which has tricarbonyl molybdenum and tetracarbonyl molybdenum unit. The formation was also confirmed by EDX study. Possible structure of 2^{Py} estimated by MM2 calculation has been shown in Fig. 4. This complex has two different environment carbonyl units. Therefore, FT-IR spectrum of $\mathbf{2}^{\mathbf{Py}}$ is completely different from those of **1^H**, **1^{Py}**, and **2^H**. (A sharp peak at 2007 cm⁻¹ for **2^{Py}** is typical peak that can be assigned to tetracarbonyl complex which has not existed in other complexes 2^{R} .) The $v(C \equiv 0)$ values of 1^{H} are similar to those of 1^{Py} and 2^H. Therefore, the structure of 1^H is expected to be similar to the structures of **1**^{Py} and **2**^H. On the basis of the results of the v(C=0) values, the carbonyl molecules of fac-[Mo(CO)₃(TACN)] are more highly activated than those of fac-[Mo(CO)₃(TTCN)]. For 1^{Py} with the L12^{py} ligand containing S and N atoms, the v(C=0) values are close to those of $fac-[Mo(CO)_3]$ (TTCN)], although they are larger than those of fac-[Mo(CO)₃



Fig. 4. Possible structure of $[{\rm Mo(CO)_3(L14^{Py})Mo(CO)_4}]~(2^{Py})$ calculated by MM2 calculations.

(TACN)]. The $v(C \equiv 0)$ (A₁ mode) [30] value of **2^H** is between the $v(C \equiv 0)$ (A₁ mode) values of **1^H** and *fac*-[Mo(CO)₃(TTCN)]. This result suggests that the intra- and intermolecular hydrogen bonds have an effect on the activation of carbon monoxide molecules through the bonds.

4. Conclusion

We have prepared four novel molybdenum tricarbonyl complexes with monoaza-trithia-macrocyclic ligands and characterized these complexes by X-ray structural and FT-IR analyses. It has been found that the intra- and intermolecular hydrogen bonds control the structural conformation around metal center, and that these hydrogen bonds contribute to regulating the v(CO) value of carbon monoxide molecules coordinated to the metal. This may indicate that hydrogen bond networks play an important role in the control of electronic and structural properties of metal center.

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Appendix A. Supplementary material

CCDC 896087 and 896088 contain the supplementary crystallographic data for compounds **1**^{Py} and **2**^H, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/ cif. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2013.03. 027.

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