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Mixed Chloride/Amine Complexes of Dimolybdenum(II,II). 4. Rotational Isomers of $\text{Mo}_2\text{Cl}_4(\text{R-py})_4$ (R-py = 4-Picoline, 3,5-Lutidine, and 4-*tert*-Butylpyridine)

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The quadruply bonded dimolybdenum complexes with alkyl-substituted pyridines of the formula $\text{Mo}_2\text{Cl}_4(\text{R-py})_4$ (R-py = 4-pic (4-methylpyridine) (**1**), 3,5-lut (3,5-dimethylpyridine) (**2**), and 4-Bu^t-py (4-*tert*-butylpyridine) (**3**)) have been prepared. Nine different compounds, in which there are 11 independent molecules, have been obtained in crystalline form, and their crystal structures have been investigated by X-ray diffraction. Three types of geometric isomers which differ by the angle of internal rotation about the Mo–Mo axis have been recognized in these structures. The eclipsed structures **1–3a** display pyridine ligands opposite to each other across the metal–metal bond and have a virtual symmetry D_{2h} . The noncentrosymmetric D_{2d} structures **1–3b** have each pyridine ligand opposite to a Cl atom. The molecules **3c–f** have a partially staggered D_2 geometry with N–Mo–Mo–N torsion angles ranging from 10.4° to 25.2°. As a result of this work it is now clear that $\text{Mo}_2\text{Cl}_4(\text{R-py})_4$ compounds do not show a preference for D_{2h} conformation rather than D_{2d} conformation. In fact, they seem unusually unrestricted in their rotational conformation, and packing forces appear to have a major influence on the conformation adopted. Further clarification of this question will require spectroscopic study of solutions.

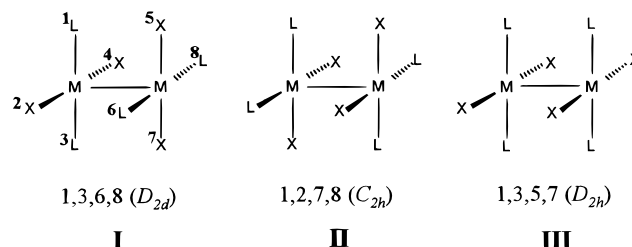
Introduction

Many molecules of composition $\text{M}_2\text{X}_4\text{L}_4$ are known in which M_2 is a multiply bonded dimetal unit, with M = Mo, W, Tc, or Re, X is an anion, such as F, Cl, Br, I, OR, or R, and L is a neutral ligand, such as a phosphine or an amine. Thus far, only three geometrical isomers of such molecules have been observed. These are shown in Chart 1.

The overwhelming majority of these compounds¹ have the structure **I**. It seems likely that this isomer is favored for steric reasons, because the L ligands are generally more sterically demanding than the X ligands and in this isomer they distance themselves from each other to the maximum possible extent. Relatively recently² it has been shown that dirhenium compounds (X = Cl; L = PMe_3 , PMe_2Ph , PET_2H) of type **II** can be made, and there is also one molybdenum compound, $\text{Mo}_2(\text{OC}_6\text{F}_5)_4(\text{PMe}_3)_4$, of this kind.³ It should be noted that isomers **I** and **II** of a given compound are not interconvertible without breaking and re-forming bonds, so that, while one isomer must be only metastable relative to the other, either or both can persist in solution as well as in the solid state.

Isomer **III** is known only for certain $\text{Mo}_2\text{X}_4(\text{R-py})_4$ compounds, where X = Cl or Br and R-py represents an alkyl-substituted pyridine. The first two such complexes (with R-py = 4-picoline and X = Cl, Br) were reported by Brenčič et al.,⁴ and another one (R-py = 4-*tert*-butylpyridine and X = Br) was reported later by Ewing et al.⁵ This structure might

Chart 1



also be expected to be less stable than **I** on steric grounds, and, moreover, **I** and **III** can easily interconvert by internal rotation about the Mo–Mo bond, where the rotation barrier⁶ is expected to be no more than about 12–13 kcal·mol^{–1}. In view of the fact that all other $\text{M}_2\text{X}_4\text{N}_4$ (N represents any amine) compounds (M = Mo,⁷ W,⁸ and N = NH_2R ; M = Mo,⁹ and N = NHR_2) have structure **I** and that the internal angles and distances in all $\text{M}_2\text{X}_4\text{N}_4$ compounds are rather similar, the absence of structure **III** in such compounds *except* when N = R-py, and the absence of any reported R-py compound with a structure other than **III**, motivated us to look further at the $\text{Mo}_2\text{X}_4(\text{R-py})_4$ compounds to see if we could understand their preference for structure **III**.

We have, therefore, attempted to prepare more such compounds by employing our previously reported synthetic methods.^{7b,8,9} We report here the isolation and crystal structure for the 1,3,5,7 (D_{2h}) isomers of $\text{Mo}_2\text{Cl}_4(4\text{-pic})_4$ (**1a**), $\text{Mo}_2\text{Cl}_4(3,5\text{-lut})_4$ (**2a**), and $\text{Mo}_2\text{Cl}_4(4\text{-Bu}^t\text{-py})_4$ (**3a**); the corresponding

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Table 1. Crystallographic Data for 1,3,5,7-Mo₂Cl₄(4-pic)₄·CHCl₃ (**1a**·CHCl₃), (*D*_{2h}), 1,3,6,8-Mo₂Cl₄(4-pic)₄ (**1b**) (*D*_{2h}), 1,3,5,7-Mo₂Cl₄(3,5-lut)₄ (**2a**) (*D*_{2h}), and 1,3,6,8-Mo₂Cl₄(3,5-lut)₄ (**2b**) (*D*_{2h})

	1a ·CHCl ₃	1b	2a	2b
formula	Mo ₂ Cl ₄ N ₄ C ₂₅ H ₂₉	Mo ₂ Cl ₄ N ₄ C ₂₄ H ₂₈	Mo ₂ Cl ₄ N ₄ C ₂₈ H ₃₆	Mo ₂ Cl ₄ N ₄ C ₂₈ H ₃₆
fw	825.55	706.18	762.29	762.29
space group	<i>C2/c</i> (No. 15)	<i>P1</i> (No. 2)	<i>P2₁/c</i> (No. 14)	<i>Pnnb</i> (No. 52)
<i>a</i> , Å	15.1436(6)	9.2958(3)	14.838(1)	13.738(2)
<i>b</i> , Å	10.7205(5)	10.2669(7)	14.762(1)	14.0856(5)
<i>c</i> , Å	19.866(1)	16.254(3)	14.434(2)	16.686(3)
α, deg		91.90(1)		
β, deg	104.579(6)	104.25(2)	90.670(8)	
γ, deg		110.458(8)		
<i>V</i> , Å ³	3121.3(2)	1396.5(3)	3161.4(5)	3228.9(8)
<i>Z</i>	4	2	4	4
ρ _{calcd} , g·cm ⁻³	1.757	1.679	1.602	1.568
μ, mm ⁻¹	1.426	1.301	1.156	1.132
radiation (λ, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
temp, °C	−60	−60	−60	−60
R1, ^a wR2 ^b [<i>I</i> > 2σ(<i>I</i>)]	0.0482, 0.1155	0.0463, 0.1237	0.0341, 0.0795	0.0456, 0.1049
R1, ^a wR2 ^b (all data)	0.0568, 0.1253	0.0548, 0.1337	0.0405, 0.0855	0.0603, 0.1168

$$^a R1 = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b wR2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}.$$

Table 2. Crystallographic Data for Different Rotational Isomers of Mo₂Cl₄(4-Bu^t-py)₄ (**3**)

	3a ·C ₆ H ₆	3ab ·2/3THF	3c ·3/4C ₆ H ₁₄	3de ·4/3CH ₂ Cl ₂	3f ·C ₆ H ₆
formula	Mo ₂ Cl ₄ N ₄ C ₄₂ H ₅₈	Mo ₂ Cl ₄ N ₄ O _{0.67} C _{38.67} H _{57.33}	Mo ₂ Cl ₄ N ₄ C _{40.5} H _{62.5}	Mo ₂ Cl ₄ N ₄ C _{37.33} H _{54.67}	Mo ₂ Cl ₄ N ₄ C ₄₂ H ₅₈
fw	952.60	922.57	939.13	987.73	952.60
space group	<i>P1</i> (No. 2)	<i>Pbca</i> (No. 61)	<i>P2₁/n</i> (No. 14)	<i>C2/c</i> (No. 15)	<i>C2/c</i> (No. 15)
<i>a</i> , Å	11.6160(2)	25.7267(9)	15.001(1)	26.504(4)	21.085(3)
<i>b</i> , Å	13.120(2)	15.6628(8)	15.261(1)	18.069(3)	19.003(4)
<i>c</i> , Å	17.071(2)	32.236(3)	21.785(1)	32.760(4)	11.577(1)
α, deg	67.950(4)				
β, deg	82.537(4)		103.790(6)	110.52(1)	101.432(9)
γ, deg	68.231(5)				
<i>V</i> , Å ³	2239.2(4)	12990(2)	4843.5(5)	14693(4)	4547(1)
<i>Z</i>	2	12	4	12	4
ρ _{calcd} , g·cm ⁻³	1.413	1.415	1.288	1.340	1.392
μ, mm ⁻¹	0.831	0.858	0.768	0.903	0.819
radiation (λ, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
temp, °C	−60	−60	−60	−60	−60
R1, ^a wR2 ^b [<i>I</i> > 2σ(<i>I</i>)]	0.0422, 0.1003	0.0439, 0.1020	0.0551, 0.1342	0.0932, 0.2327	0.0376, 0.0843
R1, ^a wR2 ^b (all data)	0.0508, 0.1103	0.0531, 0.1128	0.0740, 0.1552	0.1303, 0.2771	0.0442, 0.0899

$$^a R1 = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b wR2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}.$$

1,3,6,8 (*D*_{2d}) isomers for the same compounds (**1b**, **2b**, and **3b**, respectively); and several rotational conformers (*D*₂) with partially staggered geometry for Mo₂Cl₄(4-Bu^t-py)₄ (**3c**–**3f**).

Experimental Section

General Procedures. All manipulations were carried out under an atmosphere of dry oxygen-free argon or nitrogen with standard Schlenk techniques. Solvents were dried and deoxygenated by refluxing over suitable reagents before use. Chemicals were obtained from the following sources: Aldrich Inc. (diethylamine, 4-*tert*-butylpyridine, and NaBEt₃H), Lancaster Synthesis, Inc. (4-picoline and 3,5-lutidine), and Cambridge Isotope Laboratories, Inc. (deuterated benzene and chloroform); they were used as received. Mo₂Cl₆(THF)₃¹⁰ and Mo₂Cl₄-(NHET₂)₄⁹ were synthesized according to published procedures. Sodium amalgam was prepared in a drybox by dissolving a weighed amount of metallic sodium in an approximately measured quantity of mercury that was pumped under vacuum for at least 1 h in a Schlenk flask.

Synthesis of Mo₂Cl₄(4-pic)₄ (1**).** To a purple solution of 0.315 g (0.50 mmol) of Mo₂Cl₄(NHET₂)₄ in 15 mL of benzene was added 0.5 mL (5.10 mmol) of 4-picoline. The color of the solution changed to green; after a few minutes, red, microcrystalline material started to precipitate. The solid was filtered and recrystallized from a dichloromethane/hexanes mixture and dried under reduced pressure. Yield: 0.28 g (81%). Anal. Calcd for Mo₂Cl₄N₄C₂₄H₂₈: C, 40.82; H, 4.00; N, 7.93. Found: C, 40.54; H, 3.98; N, 7.66. IR (KBr, cm⁻¹): 3078 (w),

1620 (vs), 1502 (m), 1437 (m), 1380 (w), 1234 (m), 1220 (m), 1102 (m), 1068 (m), 1023 (m), 865 (w), 810 (s), 721 (w), 545 (w), 595 (m). ¹H NMR data (CDCl₃, 22 °C): δ 9.29 (m, 8H), 7.12 (m, 8H), 2.38 (s, 12H). UV–vis [λ_{max}, nm (Nujol)]: 580 (δ–δ* transition).

Large red, block-shaped crystals of **1a**·CHCl₃ were obtained by layering hexanes over a green solution of the compound in chloroform at room temperature. Green needles of **1b** were deposited when dichloromethane was used instead of chloroform.

Isomer **1a** undergoes a transformation to **1b** upon losing the molecule of solvation. When microcrystalline red powder of **1a** was kept under vacuum or was stirred in diethyl ether (where a suspension with an absolutely colorless liquid phase is formed), its color changed to green. This green solid was identified as **1b** by X-ray powder diffraction.

Synthesis of Mo₂Cl₄(3,5-lut)₄ (2**). Method 1.** The same procedure as in the preparation of **1** was followed except in this case 0.75 mL (6.5 mmol) of 3,5-lutidine was added to a solution of 0.10 g (0.16 mmol) of Mo₂Cl₄(NHET₂)₄ in 40 mL of toluene. After 20 min of stirring at room temperature, the solvent was removed, leaving a red-violet residue, which was washed with 25 mL of hexanes and dried under vacuum. Yield: 0.055 g (46%).

Method 2. A better result was obtained when Mo₂Cl₄(4-pic)₄ (**1b**) (0.27 g, 0.38 mmol) was treated with 7.5 mL of 3,5-lutidine. Within 10 min the color of the solid changed from green to red-brown. This product was filtered off and dried at reduced pressure overnight. Yield: 0.195 g (67%). Anal. Calcd for Mo₂Cl₄N₄C₂₈H₃₆: C, 44.12; H, 4.76; N, 7.35. Found: C, 43.92; H, 4.63; N, 7.27. IR (KBr, cm⁻¹): 3082 (m), 2954 (w), 2917 (m), 2862 (m), 1598 (m), 1458 (br.s), 1379 (w), 1329 (w), 1240 (w), 1182 (m), 1151 (vs), 1041 (m), 869 (m), 806

Table 3. Selected Bond Distances (Å), Angles (deg), and Torsion Angles (deg) for Mo₂Cl₄(4-pic)₄ (**1a** and **1b**) and Mo₂Cl₄(3,5-lut)₄ (**2a** and **2b**)

	1a-CHCl ₃	1b		2a		2b
Mo–Mo	2.143(1)	2.1497(9)		2.1421(6)		2.139(1)
Mo–N	2.232(6)	2.254(6)	2.237(6)	2.243(3)	2.247(3)	2.262(5)
	2.244(5)	2.247(6)	2.243(6)	2.239(3)	2.255(3)	2.255(5)
Mo–Cl	2.419(2)	2.421(2)	2.414(2)	2.424(1)	2.418(1)	2.411(2)
	2.419(2)	2.417(2)	2.398(2)	2.404(1)	2.423(1)	2.401(2)
N–Mo–N	156.9(2)	159.5(2)	155.3(2)	159.1(1)	155.0(1)	164.9(2)
Cl–Mo–Cl	147.82(7)	146.13(7)	145.00(7)	146.12(4)	148.79(4)	139.64(6)
N–Mo–Cl	87.7(1)	84.5(2)	87.8(2)	83.30(9)	89.25(9)	87.0(1)
	86.8(2)	90.6(2)	83.6(2)	89.3(1)	89.50(9)	87.7(1)
	86.8(2)	88.4(1)	84.8(2)	85.52(9)	83.22(9)	87.7(1)
	86.0(2)	84.7(2)	89.0(2)	90.20(9)	85.01(9)	87.2(1)
Mo–Mo–N	101.2(1)	99.3(1)	102.6(2)	101.01(9)	101.83(9)	97.7(1)
	101.8(1)	101.1(1)	102.1(2)	99.46(9)	102.79(9)	97.4(1)
Mo–Mo–Cl	105.98(6)	106.67(5)	107.72(5)	110.26(3)	102.48(3)	110.44(5)
	106.19(6)	107.20(5)	107.26(5)	103.60(3)	108.70(3)	109.92(5)
N–Mo–Mo–N _{av}	0.9(2)			4.4(1)		
Cl–Mo–Mo–Cl _{av}	0.71(8)			0.16(4)		
N–Mo–Mo–Cl _{av}		9.0(2)				9.4(1)

Table 4. Selected Bond Distances (Å), Angles (deg), and Torsion Angles (deg) for Mo₂Cl₄(4-Bu^t-py)₄ (**3a–f**)

	3a		3a		3b		3c		3d		3e	3f
Mo–Mo	2.1423(5)		2.1401(8)		2.1382(6)		2.1413(8)		2.136(2)		2.150(2)	2.1570(8)
Mo–N	2.232(4)	2.235(4)	2.237(4)	2.244(4)	2.236(4)	2.227(5)	2.234(6)	2.25(1)	2.22(1)	2.23(1)	2.239(3)	
	2.235(4)	2.233(4)	2.249(4)	2.250(4)	2.243(4)	2.230(5)	2.228(6)	2.25(1)	2.23(1)	2.22(1)	2.237(3)	
Mo–Cl	2.429(1)	2.416(1)	2.415(1)	2.424(1)	2.415(1)	2.408(2)	2.434(2)	2.403(3)	2.412(4)	2.419(3)	2.411(1)	
	2.412(1)	2.431(1)	2.412(1)	2.410(1)	2.410(1)	2.416(2)	2.406(2)	2.423(4)	2.419(4)	2.416(4)	2.407(1)	
N–Mo–N	158.4(1)	153.2(1)	156.4(1)	163.0(1)	159.2(2)	153.9(2)	158.3(2)	157.7(4)	156.9(4)	160.5(4)	162.3(1)	
Cl–Mo–Cl	147.00(4)	149.32(4)	146.80(5)	142.33(5)	143.34(5)	148.78(7)	147.77(7)	149.5(1)	149.7(2)	146.1(1)	144.93(5)	
N–Mo–Cl	84.0(1)	89.08(9)	89.6(1)	88.3(1)	88.2(1)	82.7(1)	89.2(1)	85.5(3)	87.6(3)	87.9(3)	90.16(9)	
	89.0(1)	82.88(9)	84.3(1)	86.4(1)	88.9(1)	88.4(1)	84.9(2)	88.2(3)	84.3(3)	85.0(3)	89.91(9)	
	85.4(1)	90.17(9)	89.1(1)	85.5(1)	88.2(1)	89.3(1)	85.4(2)	88.9(3)	85.5(3)	84.8(3)	82.41(9)	
	89.72(9)	84.22(9)	83.9(1)	88.9(1)	81.8(1)	85.7(1)	88.6(2)	85.7(3)	90.5(3)	91.1(3)	89.97(9)	
Mo–Mo–N	100.78(9)	103.9(1)	100.9(1)	98.4(1)	100.9(2)	104.1(1)	99.9(2)	101.7(3)	103.5(3)	101.1(3)	97.19(9)	
	100.41(9)	102.40(9)	102.3(1)	98.7(1)	102.3(1)	102.0(1)	101.8(1)	100.6(3)	99.6(3)	98.3(3)	100.39(9)	
Mo–Mo–Cl	108.90(3)	101.94(3)	103.77(4)	110.10(4)	107.65(4)	104.75(5)	107.27(5)	104.6(1)	104.5(1)	107.5(1)	107.45(3)	
	104.09(3)	108.73(3)	109.44(4)	107.57(4)	108.93(4)	106.44(5)	104.96(6)	105.9(1)	105.8(1)	106.4(1)	107.59(3)	
N–Mo–Mo–N _{av}	0.7(1)		0.0(2)			10.4(2)		15.4(4)		21.5(6)		25.2(1)
Cl–Mo–Mo–Cl _{av}	0.52(5)		0.00(6)			5.99(7)		11.7(2)		16.6(1)		19.47(6)
N–Mo–Mo–Cl _{av}					4.5(1)							

(w), 758 (m), 697 (m). ¹H NMR data (CDCl₃, 22 °C): δ 9.01 (m, 8H), 7.16 (m, 4H), 2.17 (m, 24H). UV–vis [λ_{max} , nm (Nujol)]: 560 (δ–δ* transition).

A green solution of the compound in dichloromethane was layered with diethyl ether at room temperature. The following day red (**2a**) and pale brown (**2b**) block-shaped crystals were formed. The same mixture of crystals was obtained when chloroform instead of dichloromethane was used. However, from a benzene/hexanes layering system only crystals of **2b** could be deposited when the diffusion process was not allowed to be completed.

Synthesis of Mo₂Cl₄(4-Bu^t-py)₄ (3**). Method 1.** Essentially the same procedure as in the preparation described for compound **1** was employed using 0.12 g (0.19 mmol) of Mo₂Cl₄(NHEt₂)₄ in 5 mL of benzene and 0.3 mL (2.02 mmol) of 4-Bu^t-py. The volatile components of the reaction solution were evaporated under reduced pressure, and the dark brown-violet residue was washed with 25 mL of hexanes. Yield: 0.12 g (72%).

Method 2. A flask which contained a suspension of 0.15 g (0.24 mmol) of Mo₂Cl₆(THF)₃ in 10 mL of THF was kept sunk in a dry ice/ethanol bath. The 4-Bu^t-py (1 mL, 6.73 mmol) and 2 equiv of Na/Hg (0.4%) were added to the flask, and the mixture was allowed to reach room temperature slowly (2 h). The suspension was filtered, and the resulting dark brown-violet solution was evaporated to dryness. The brown-violet compound was extracted with 30 mL of toluene, and the solvent was removed under vacuum. Yield: 0.10 g (47%). Anal. Calcd for Mo₂Cl₄N₄C₃₆H₅₂: C, 49.44; H, 5.99; N, 6.41. Found: C, 48.99; H, 6.03; N, 6.37. IR (Nujol, cm⁻¹): 1616 (s), 1541 (w), 1498

(m), 1418 (m), 1367 (sh), 1301 (w), 1274 (sh), 1261 (s), 1231 (m), 1201 (w), 1168 (w), 1095 (vs), 1065 (vs), 1021 (vs), 865 (w), 843 (m), 830 (vs), 802 (vs), 750 (w), 723 (m), 683 (w), 668 (w), 570 (vs), 543 (w), 476 (br, w). ¹H NMR data (benzene-*d*₆, 22 °C): δ 9.99 (m, 8H), 6.89 (m, 8H), 0.92 (s, 36H). UV–vis [λ_{max} , nm (Nujol)]: 555 (δ–δ* transition).

Red plate-shaped crystals of **3a**·C₆H₆, along with green plates of **3c**·C₆H₁₄, were grown by layering hexanes over a saturated solution of the compound in benzene at room temperature. Red block-shaped crystals of cocrystallized isomers **3b** and **3a** solvated with THF were formed by layering hexanes over a concentrated solution of **3** in THF. When a concentrated solution of **3** in dichloromethane was evaporated very slowly by passing a stream of nitrogen, green needles were obtained which contained **3d** and **3e** solvated with dichloromethane. Green needles of the conformer **3f** solvated with benzene were deposited after 1 week when a concentrated solution of **3** in 5 mL of benzene and 3 mL of free 4-Bu^t-py was layered with hexanes.

Physical Measurements. Infrared spectra were recorded on a Perkin-Elmer 16PC FTIR spectrometer using suspensions of the compounds in Nujol or on an ATI Mattson Genesis FTIR employing KBr pellets. ¹H NMR spectra were obtained on a Varian XL-200E spectrometer; internal standard resonances were CHCl₃, 7.24 ppm, and C₆D₅H, 7.15 ppm. Visible spectra of Nujol mulls of the complexes were acquired using a Cary-17D UV–vis spectrophotometer. X-ray powder diffraction experiments were performed on Rigaku automated diffractometer (monochromatized Cu K α_1 radiation). Elemental analyses were done by Canadian Microanalytical Services, Ltd.

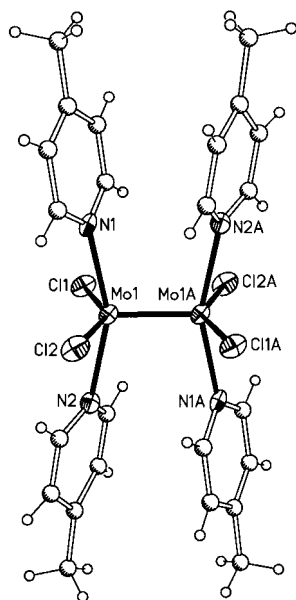


Figure 1. Perspective drawing of the D_{2h} isomer of $\text{Mo}_2\text{Cl}_4(4\text{-pic})_4$ (**1a**). Atoms are represented by thermal ellipsoids at the 40% probability level. For clarity carbon and hydrogen atoms are shown as spheres of arbitrary radii and not labeled.

X-ray Crystallographic Procedures. Single crystals of compounds **1–3** were obtained as described above. The X-ray diffraction experiments were carried out on a Nonius FAST diffractometer with an area detector using Mo $K\alpha$ radiation. In each case, a crystal of suitable quality was affixed to the end of a quartz fiber with grease in a cold nitrogen stream (-60°C). Unit cell determination and data collection followed routine procedures and practices of this laboratory.¹¹ Oscillation photographs of principal axes were taken to confirm the Laue class and axial lengths. All data were corrected for Lorentz and polarization effects. The structures were solved and refined using the SHELXTL direct methods¹² and the SHELXL-93 programs¹³ on a DEC Alpha running VMS. In each model, the hydrogen atoms were included in the structure factor calculations at idealized positions. Relevant crystallographic data for complexes **1–3** are summarized in Tables 1 and 2.

Orientational disorder was encountered in several cases. All or some Bu^i groups were disorder over two or three rotational orientations in the crystal structures of rotational isomers **3**. Two orientations of the aromatic rings were found in **1a**· CHCl_3 . Also, all interstitial solvent molecules, except THF in **3ab**, were severely disordered.

Results and Discussion

We have made nine distinct substances, that is, compounds with nine different crystal structures, two with R-py = 4-picoline, two with R-py = 3,5-lutidine, and five with R-py = 4-*tert*-butylpyridine. These compounds and their crystallographic characteristics as well as the conditions and figures of merit for the structure determination are presented in Tables 1 and 2.

In these nine different substances there are 11 crystallographically distinct molecules. These are presented in Tables 3 and 4. It can be seen that over these 11 different molecules there is hardly any variation in dimensions with the sole exception of the angle of internal rotation about the Mo–Mo axis. In addition to some molecules of type **III**, we have three that are close to type **I** and others that are in between.

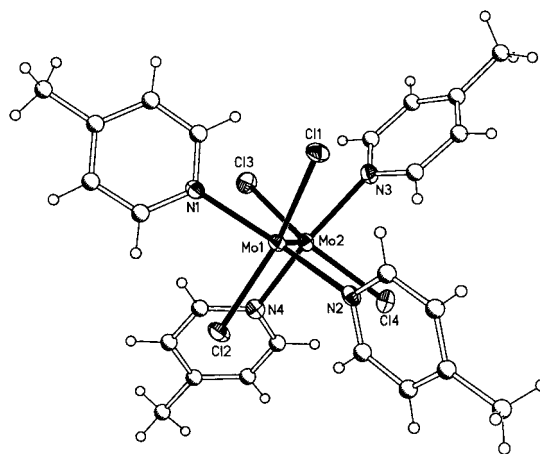


Figure 2. Perspective drawing of the D_{2d} isomer of $\text{Mo}_2\text{Cl}_4(4\text{-pic})_4$ (**1b**). Atoms are represented by thermal ellipsoids at the 40% probability level. For clarity carbon and hydrogen atoms are shown as spheres of arbitrary radii and not labeled.

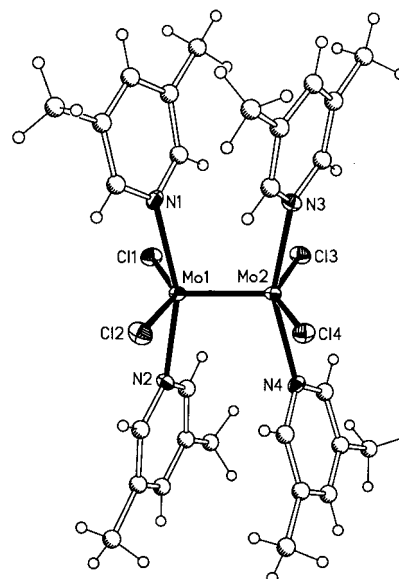


Figure 3. Perspective drawing of the D_{2h} isomer of $\text{Mo}_2\text{Cl}_4(3,5\text{-lut})_4$ (**2a**). Atoms are represented by thermal ellipsoids at the 40% probability level. For clarity carbon and hydrogen atoms are shown as spheres of arbitrary radii and not labeled.

In Figures 1–7 the structures of some of these molecules are shown. For each type of R-py ligand, Figures 1/2, 3/4, and 5/6 show the D_{2h}/D_{2d} isomers. Thus, it is clear that the ability of these molecules to exist in both of the eclipsed forms is independent of the R-py ligand used. Figure 7 shows a representative D_2 structure, namely, that of **3f**, where there are the greatest deviation from a D_{2h} form of eclipsed bonds and the longest Mo–Mo bond distance among title compounds. Figure 8 shows a selection of the 11 structures with D_{2h} , D_2 , and D_{2d} structures where the emphasis is on the appearance of the conformation as viewed down the Mo–Mo axis.

In order to arrange the 11 molecular structures for discussion we adopt the following three categories:

(1) Structures that are of type **III** or close to it (N–Mo–Mo–N torsion angles of 0 – 4.4°) will be designated D_{2h} structures. There are four of these, **1a**, **2a**, and two examples of **3a**. One of the latter is rigorously D_{2h} with a torsion angle of exactly 0° , but the others are very close.

(2) Structures that are of type **I** or close to it, namely, **1b**, **2b**, and **3b**, have N–Mo–Mo–Cl torsion angles in the range

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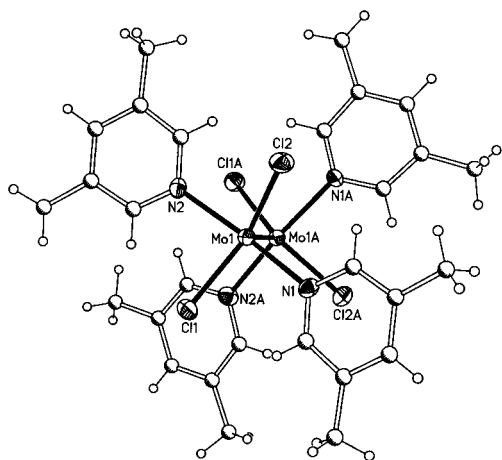


Figure 4. Perspective drawing of the D_{2d} isomer of $\text{Mo}_2\text{Cl}_4(3,5\text{-lut})_4$ (**2b**). Atoms are represented by thermal ellipsoids at the 40% probability level. For clarity carbon and hydrogen atoms are shown as spheres of arbitrary radii and not labeled.

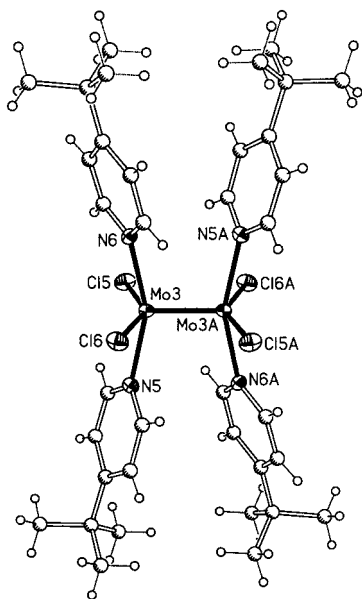


Figure 5. Perspective drawing of the D_{2h} isomer of $\text{Mo}_2\text{Cl}_4(4\text{-Bu}^i\text{-py})_4$ (**3a**). Atoms are represented by thermal ellipsoids at the 40% probability level. For clarity carbon and hydrogen atoms are shown as spheres of arbitrary radii and not labeled.

$4.5\text{--}9.4^\circ$. Thus, while none are rigorously of symmetry D_{2d} , we shall refer to them all as D_{2d} structures.

(3) Structures that are outside the ranges for categories 1 and 2 have N—Mo—Mo—N torsion angles in the range $10.4\text{--}25.2^\circ$. We shall designate these as D_2 structures, and there are four of them, **3c–f**.

Instances of rotational isomerism are rare, and this is by far the most spectacular array. The only prior examples of which we are aware are (1) $[\text{Mo}_2\text{Br}_6(\text{H}_2\text{O})_2]^{2-}$, which forms eclipsed structures with both C_{2h} and C_2 conformations,¹⁴ and (2) $[\text{Re}_2\text{Cl}_6(\text{PPR}^i)_2]^-$, which is known with C_{2h} and C_2 symmetries.¹⁵ There is no prior example of such isomerism for any $\text{M}_2\text{X}_4\text{L}_4$ species.

The molecule **3f** has the distinction of displaying the largest deviation from eclipsed rotational geometry (see Table 4) of

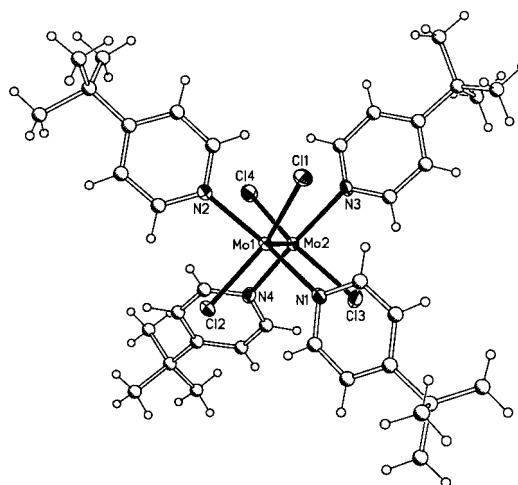


Figure 6. Perspective drawing of the D_{2d} isomer of $\text{Mo}_2\text{Cl}_4(4\text{-Bu}^i\text{-py})_4$ (**3b**). Atoms are represented by thermal ellipsoids at the 40% probability level. For clarity carbon and hydrogen atoms are shown as spheres of arbitrary radii and not labeled.

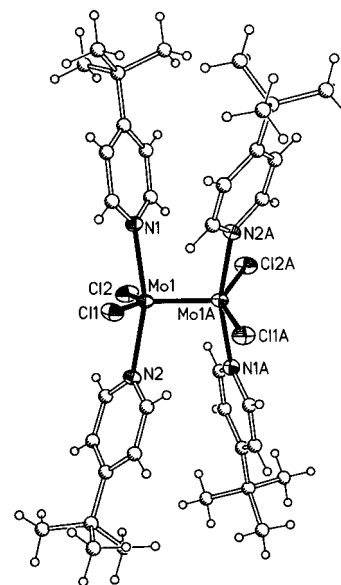


Figure 7. Perspective drawing of the D_2 isomer of $\text{Mo}_2\text{Cl}_4(4\text{-Bu}^i\text{-py})_4$ (**3f**). Atoms are represented by thermal ellipsoids at the 40% probability level. For clarity carbon and hydrogen atoms are shown as spheres of arbitrary radii and not labeled.

any known quadruply bonded dimolybdenum molecule in which all ligands are monodentate. Of course, in various $\text{Mo}_2\text{X}_4(\text{P-P})_2$ molecules even larger deviations are found,¹⁶ but these are caused by the conformational demands of the fused Mo—P—P—Mo rings.

It is also quite novel to find substances in which there are independent molecules with the same composition but different conformations, as in the case with **3ab** and **3de**. The only earlier examples we know of are $\text{Mo}_2\text{I}_4(\text{P-P})_2$ compounds.¹⁷ A related,

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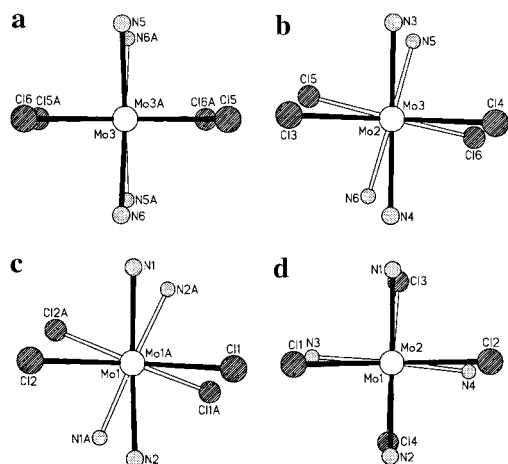


Figure 8. Views of the central part of the molecules $\text{Mo}_2\text{Cl}_4(4\text{-Bu}^t\text{-py})_4$ (a) **3a**, (b) **3d**, (c) **3f**, and (d) **3b**, directly down the Mo–Mo axis. Atoms are represented as spheres of arbitrary radii. Only molybdenum and its neighboring atoms are depicted. For the torsion angles, see Table 4.

but not the same, phenomenon is the cocrystallization of the 1,2,7 and 1,3,6 isomers of $\text{Re}_2\text{Cl}_5(\text{PMe}_3)_3$.¹⁸

The most obvious message from this body of results is that, after all, the D_{2h} structure is not especially favored, as might have appeared to be the case on the basis of the limited earlier literature,^{4,5} where it was the only structure to show up. The true picture seems to be that the internal rotational barriers in these molecules do not strongly favor any particular conformation and therefore the crystal packing forces play an important role and can determine the result.

The lack of any strong inherent conformational preference is in contrast to the situation in $\text{Mo}_2\text{X}_4(\text{PR}_3)_4$ molecules, where the relatively large size of the PR_3 ligands engenders a strong preference for a type **I** structure rather than a type **III** structure.

On the basis of the larger sample now in hand, we see that the numbers of type **I** and **III** structures are not greatly different. When the neutral ligands are substituted pyridines rather than phosphines, it could well be that $\text{Cl}\cdots\text{Cl}$ repulsions are comparable in magnitude to $\text{py}\cdots\text{py}$ repulsions and $\text{py}\cdots\text{Cl}$ repulsions. Rank ordering these three is not easy because there are other factors besides size that must be considered. In the type **III** conformation it is possible that an attractive stacking force between the aromatic rings makes some contribution. On the other hand dipolar interactions involving Mo–N and Mo–Cl bonds (presumably of opposite polarities) could favor structure **I** over **III**.

The appearance of a range of D_2 structures could mean that the tendency of the δ -bonding to favor one or the other (**I** or **III**) of the completely eclipsed structures is easily offset by the nonbonded ligand–ligand interactions, but on the other hand these D_2 structures could result mainly from packing interactions.

The present position is that we now know that the question of what rotamer or rotamers are preferred by an $\text{Mo}_2\text{Cl}_4(\text{R-py})_4$ molecule, and why, is now open to a variety of answers. However, to make further progress, methods other than crystallography must be used. Among these are various forms of spectroscopy and theory. We are currently engaged in such studies and will report our results presently.¹⁹

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Supporting Information Available: Nine X-ray crystallographic files, in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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