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Mixed Chloride/Amine Complexes of Dimolybdenum(II,II). 3. Preparation, Characterization, and Crystal Structure of $\text{Mo}_2\text{Cl}_4(\text{NH}_2\text{R})_4$ ($\text{R} = \text{Et}, \text{Pr}^n, \text{Bu}^t, \text{Cy}$): First Quadruply-Bonded Dimolybdenum Compounds with Primary Amine Ligands

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Four new quadruply-bonded dimolybdenum(II) complexes of the formula $\text{Mo}_2\text{Cl}_4(\text{NH}_2\text{R})_4$ ($\text{R} = \text{Et}$ (**1**), Pr^n (**2**), Bu^t (**3**), Cy (**4**)) have been prepared in excellent yield by reduction of the dimolybdenum(III) complex $\text{Mo}_2\text{Cl}_6(\text{THF})_3$ with 2 equiv of sodium amalgam in the presence of the appropriate primary amine. The molecular structures of **2–4** have been investigated by X-ray crystallography. Crystal data are as follows: for **2**, orthorhombic space group $Ccca$ with $a = 13.328(3) \text{ \AA}$, $b = 26.639(5) \text{ \AA}$, $c = 6.774(2) \text{ \AA}$, and $Z = 4$; for **3**, monoclinic space group $P2_1/c$ with $a = 19.165(1) \text{ \AA}$, $b = 20.858(1) \text{ \AA}$, $c = 14.1400(8) \text{ \AA}$, $\beta = 99.002(5)^\circ$, and $Z = 8$; for **4**, tetragonal space group $P4_22_12$ with $a = 15.556(4) \text{ \AA}$, $c = 6.9368(8) \text{ \AA}$, and $Z = 2$. All of the non-centrosymmetric molecules **2–4** possess the same structure characterized by a $\text{Mo}_2\text{Cl}_4\text{N}_4$ core with D_{2d} virtual symmetry and slight deviation from the eclipsed geometry. The Mo–Mo bond lengths for **2**, **3**, and **4** are 2.118(2), 2.1322(6), and 2.117(1) \AA , respectively, which are consistent with the Mo–Mo quadruple bond. In addition to the structural data, IR, UV–vis, and ^1H NMR spectroscopy have been used to characterize the complexes **1–4**. Without amalgam, the reactions of the starting material with amines also produce the reduced species but with low yields (not exceeding 25%). The main products of these interactions have been found to be mononuclear molybdenum(III) complexes $\text{MoCl}_3(\text{NH}_2\text{R})_3$. This has been confirmed by a single-crystal X-ray diffraction study for *mer*- $\text{MoCl}_3(\text{NH}_2\text{Pr}^n)_3 \cdot \frac{1}{6}\text{THF}$ (**2a**· $\frac{1}{6}\text{THF}$) with the following crystal data: triclinic space group $P\bar{1}$, $a = 12.370(2) \text{ \AA}$, $b = 17.977(2) \text{ \AA}$, $c = 25.498(6) \text{ \AA}$, $\alpha = 95.32(1)^\circ$, $\beta = 103.21(2)^\circ$, $\gamma = 103.48(1)^\circ$, and $Z = 12$.

Introduction

It has recently been found¹ that the reaction of the molybdenum(III) complex $\text{Mo}_2\text{Cl}_6(\text{THF})_3$ with the secondary amine NH_2Et at room temperature causes reduction of the starting material to produce the dimolybdenum(II) complex $\text{Mo}_2\text{Cl}_4(\text{NH}_2\text{Et})_4$. The yield of the product can be significantly improved by assisted reduction with sodium amalgam. Complex $\text{Mo}_2\text{Cl}_4(\text{NH}_2\text{Et})_4$ was shown² to be an interesting starting material offering access to further chemistry of Mo_2^{4+} . In particular, the substitution reactions with bidentate phosphines led to the isolation of a new class of quadruply-bonded dimolybdenum complexes, $\text{Mo}_2\text{Cl}_4(\eta^1\text{-diphosphine})_4$.

To further study the interaction between Mo^{III} species and amines we turned to primary amines, NH_2R , which have not been used before for multiply-bonded compounds of Mo. It was found that the reaction of $\text{Mo}_2\text{Cl}_6(\text{THF})_3$ with NH_2R ($\text{R} = \text{Et}, \text{Pr}^n, \text{Bu}^t$, and Cy) gives low yields of reduced species, both at room temperature and under reflux conditions, with the major process being the deposition of mononuclear Mo^{III} complexes $\text{MoCl}_3(\text{NH}_2\text{R})_3$. However, the use of amalgam in this process results in obtaining dimolybdenum(II) compounds $\text{Mo}_2\text{Cl}_4(\text{NH}_2\text{R})_4$ in close to quantitative yields. Four new complexes $\text{Mo}_2\text{Cl}_4(\text{NH}_2\text{R})_4$ ($\text{R} = \text{Et}$ (**1**), Pr^n (**2**), Bu^t (**3**), Cy (**4**)) have been prepared and characterized by IR, UV–vis, ^1H NMR spectroscopy, and single-crystal X-ray diffraction studies.

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. NH_2Et , NH_2Pr^n , NH_2Bu^t , and NH_2Cy were purchased from Aldrich, Inc. Benzene- d_6 and chloroform- d_1 were obtained from Cambridge Isotope Laboratories, Inc., and used as received. $\text{Mo}_2\text{Cl}_6(\text{THF})_3$ was synthesized according to a published procedure.³ 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.

(A) Reactions of $\text{Mo}_2\text{Cl}_6(\text{THF})_3$ with Primary Amines and Na/Hg Amalgam. (A1) Synthesis of $\text{Mo}_2\text{Cl}_4(\text{NH}_2\text{Et})_4$ (1**).** To a suspension containing 0.15 g (0.24 mmol) of $\text{Mo}_2\text{Cl}_6(\text{THF})_3$ in a mixture of 5 mL of THF and 10 mL of CH_2Cl_2 at -78°C was added 2 equiv of sodium amalgam (0.4%). The reaction system was slowly warmed to -25°C , and then 5 mL of a 2 M solution of NH_2Et in THF was syringed in. At a temperature of -10°C another 70 mL of CH_2Cl_2 was added, and the reaction mixture was allowed to reach room temperature. It was stirred for 15 min, after which the purple solution was filtered and all volatile components were removed under reduced pressure to leave a homogeneous reddish solid. Yield: 0.08 g (65%).

Small red crystals of **1** could be obtained by layering either hexanes over a dichloromethane solution or ether over a chloroform solution.

Anal. Calcd for $\text{Mo}_2\text{Cl}_4\text{N}_4\text{C}_8\text{H}_{28}$: C, 18.69; H, 5.49; N, 10.90. Found: C, 18.44; H, 5.41; N, 10.28. IR data (KBr, cm^{-1}): 3273 (vs), 3225 (s), 2971 (s), 2928 (s), 1628 (m), 1556 (s), 1465 (m), 1381 (w), 1261 (m), 1203 (s), 1062 (br, vs), 887 (w), 801 (s), 604 (s). ^1H NMR

(1) Cotton, F. A.; Dikarev, E. V.; Herrero, S. *Inorg. Chem.* **1998**, *37*, 5862.

(2) Cotton, F. A.; Dikarev, E. V.; Herrero, S. *Inorg. Chem.* **1999**, *38*, 490.

(3) Boyd, I. W.; Wedd, A. G. *Aust. J. Chem.* **1976**, *29*, 1829.

data (CDCl₃, 22° C) δ 3.84 (br, t, NH₂), 2.76 (m, CH₂), 1.13 (t, CH₃); $J(\text{NH}_2\text{--CH}_2) = J(\text{CH}_2\text{--CH}_3) = 7$ Hz. UV-vis (THF; λ_{max} , nm): 530 ($\delta\text{--}\delta^*$ transition).

(A2) Synthesis of Mo₂Cl₄(NH₂Prⁿ)₄ (2). Two equivalents of sodium amalgam (0.4%) was added to a suspension of 0.15 g (0.24 mmol) of Mo₂Cl₆(THF)₃ in 10 mL of THF at -78 °C. The system was slowly warmed to -25 °C, and 1 mL (12 mmol) of NH₂Prⁿ was added. The reaction mixture was allowed to reach room temperature, and 50 mL of benzene was then added. After stirring for 20 min at room temperature, the purple solution was filtered and solvent was removed in vacuo, leaving a red residue. Yield: 0.11 g (80%).

Red crystals of **2** were obtained in a week by layering isomeric hexanes over a toluene solution at -30 °C.

Anal. Calcd for Mo₂Cl₄N₄C₁₂H₃₆: C, 25.28; H, 6.36; N, 9.83. Found: C, 25.57; H, 6.35; N, 9.54. IR data (KBr, cm⁻¹): 3276 (vs), 3222 (vs), 2962 (vs), 2879 (s), 1561 (s), 1468 (m), 1385 (w), 1311 (w), 1188 (s), 1070 (sh, m), 1050 (s), 1005 (m), 873 (vw), 751 (w), 606 (m). ¹H NMR data (benzene-*d*₆, 22° C): δ 4.03 (br, t, NH₂), 2.62 (m, CH₂), 1.03 (m, CH₃), 0.59 (t, CH₃); $J(\text{NH}_2\text{--CH}_2) = J(\text{CH}_2\text{--CH}_3) = 7$ Hz. UV-vis (THF; λ_{max} , nm): 528 ($\delta\text{--}\delta^*$ transition).

(A3) Synthesis of Mo₂Cl₄(NH₂Bu^t)₄ (3). A suspension of 0.15 g (0.24 mmol) of Mo₂Cl₆(THF)₃ in 5 mL of THF was cooled in an ethanol/dry ice bath. Two equivalents of sodium amalgam (0.4%) and 1 mL (9.5 mmol) of NH₂Bu^t were added to the suspension, which was then allowed to reach ambient temperature and was stirred for another 3 h. Benzene (50 mL) was added to the reaction mixture, followed by filtration. All volatile components were evaporated from the purple solution under reduced pressure to leave a red solid. Yield: 12 g (79%).

Crystals of **3** were obtained by cooling saturated solutions in hexanes or diethyl ether to -30 °C and by carefully layering isomeric hexanes over a toluene solution.

Anal. Calcd for Mo₂Cl₄N₄C₁₆H₄₄: C, 30.69; H, 7.08. Found: C, 30.93; H, 7.31. IR data (KBr, cm⁻¹): 3278 (w), 3193 (w), 3114 (vw), 2966 (vs), 1566 (m), 1473 (w), 1398 (m), 1373 (s), 1263 (vs), 1208 (s), 1127 (vs), 1100 (vs), 1025 (vs), 899 (w), 803 (vs), 636 (w). ¹H NMR data (benzene-*d*₆, 22° C): δ 4.52 (br, NH₂), 1.08 (s, CH₃). UV-vis (THF; λ_{max} , nm): 538 ($\delta\text{--}\delta^*$ transition).

(A4) Synthesis of Mo₂Cl₄(NH₂Cy)₄ (4). Procedures similar to those just described for **2** were followed to prepare Mo₂Cl₄(NH₂Cy)₄ (**4**) using cyclohexylamine (1 mL, 8.7 mmol). The red solid was isolated with a yield of 94%.

The orange-red crystals of **4** used for the X-ray experiment were obtained by keeping a saturated solution of the compound in hexanes at -30 °C for a week.

Anal. Calcd for Mo₂Cl₄N₄C₂₄H₅₂: C, 39.47; H, 7.18; N, 7.67. Found: C, 39.47; H, 6.99; N, 7.41. IR data (KBr, cm⁻¹): 3287 (m), 3238 (m), 2930 (vs), 2855 (s), 1568 (s), 1448 (m), 1388 (vw), 1344 (vw), 1261 (s), 1218 (m), 1179 (w), 1124 (s), 1100 (s), 1073 (s), 1046 (vs), 962 (w), 891 (w), 803 (s), 634 (w). ¹H NMR data (benzene-*d*₆, 22° C): δ 4.41 (d, NH₂), 3.18 (m, CH), 1.6-0.6 (CH₂); $J(\text{NH}_2\text{--CH}) = 7$ Hz. UV-vis (THF; λ_{max} , nm): 530 ($\delta\text{--}\delta^*$ transition).

(B) Reactions of Mo₂Cl₆(THF)₃ with Primary Amines without Na/Hg Amalgam at Room Temperature. **(B1) NH₂Prⁿ.** To a suspension of 0.20 g (0.32 mmol) of Mo₂Cl₆(THF)₃ in 20 mL of THF was added 0.5 mL (6.0 mmol) of NH₂Prⁿ. The mixture was stirred overnight at room temperature, and the yellow precipitate which appeared was filtered off. Another 5 mL of tetrahydrofuran was added to the red solution, and 25 mL of hexanes was layered over it. After 3 weeks, yellow crystals (0.12 g, 49%) were formed and identified by X-ray as *mer*-MoCl₃(NH₂Prⁿ)₃ (**2a**). The dinuclear complex **2**, which remained in solution, was detected by ¹H NMR.

(B2) NH₂Bu^t. To a suspension containing 0.30 g (0.48 mmol) of Mo₂Cl₆(THF)₃ in 10 mL of THF was added 2 mL (19 mmol) of NH₂Bu^t. The mixture was stirred at room temperature for 3 days. The yellow precipitate was filtered off (0.22 g, 54%) and identified as mononuclear complex MoCl₃(NH₂Bu^t)₃ (**3a**) on the basis of chemical analyses. All volatile components were evaporated from the red-brown solution, and an extraction with 50 mL of hot hexanes was made. The extract contained 0.07 g (23%) of Mo₂Cl₄(NH₂Bu^t)₄ (**3**), identified by means of ¹H NMR. The brown residue insoluble in hexanes (0.07 g, 16%)

was designated as [NH₃Bu^t][MoCl₄(NH₂Bu^t)₂] salt on the basis of chemical analyses.

(B3) NH₂Cy. A mixture of 0.30 g (0.48 mmol) of Mo₂Cl₆(THF)₃, 2 mL (17.4 mmol) of NH₂Cy, and 10 mL of THF was stirred at room temperature for 20 h to form a reddish brown solution. All volatile components were removed under reduced pressure, and an extraction was made with a mixture of 10 mL of benzene and 30 mL of hexanes. The extracted complex was shown to be Mo₂Cl₄(NH₂Cy)₄ (**4**) (0.06 g, 17%) by ¹H NMR. The residue was separated into two fractions: a brown solid soluble in benzene (0.04 g, 8%), which has not been identified, and a yellow product insoluble in benzene (0.29 g, 60%), which was identified as the mononuclear complex *mer*-MoCl₃(NH₂Cy)₃ (**4a**) by X-ray diffraction.⁴

(C) Reaction of Mo₂Cl₆(THF)₃ with NH₂Bu^t without Na/Hg Amalgam in Refluxing THF. A mixture of 0.30 g (0.48 mmol) of Mo₂Cl₆(THF)₃ and 2 mL of NH₂Bu^t (19 mmol) was refluxed in 20 mL of THF for 3 h. The reddish brown solution was then evaporated to dryness, and the complex Mo₂Cl₄(NH₂Bu^t)₄ (**3**) was extracted from the residue with 50 mL of hot hexanes and identified by ¹H NMR. Yield: 0.05 g (16%).

Physical Measurements. Infrared spectra were recorded on a Perkin-Elmer 16PC FTIR spectrometer using 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). Electronic spectral data were obtained in THF, using a Cary-17D UV-vis spectrophotometer. Thermal analysis was performed by a TA 4000 thermogravimetric unit (under nitrogen, heating rate 2.5 °C/min). Elemental analyses were done by Canadian Microanalytical Services, Ltd. (Delta, BC V4G 1G7, Canada).

X-ray Crystallographic Procedures. Single crystals of compounds **2**, **2a**, **3**, and **4** were obtained as described above. In each case, a crystal of suitable quality was affixed to the end of a quartz fiber with grease in a cold nitrogen stream (-120, -100, or -60° C). X-ray diffraction experiments were carried out using one of the two fully automated diffractometers equipped with monochromatized Mo K α radiation, Enraf-Nonius CAD-4S (**2** and **2a**) and Nonius FAST (**3** and **4**). Unit cell determination and data collection followed routine procedures and practices of this laboratory.⁵ Oscillation photographs around 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 methods⁶ and the SHELXL-93 programs⁷ on a DEC Alpha running VMS. In each model, hydrogen atoms were included at idealized positions for the structure factor calculations but were not refined. Details on data collection and structure refinement are reported in Table 1.

Mo₂Cl₄(NH₂Prⁿ)₄ (2). A red plate of dimensions 0.30 \times 0.20 \times 0.05 mm was selected for diffraction study. The ω - 2θ scan technique was used to scan data points. There was no significant decay of the crystal, as indicated by the intensity standards. An empirical absorption correction based on azimuthal scans of reflections with their ψ angles near 90° was applied. The crystal was shown to belong to the C-centered orthorhombic system, and analysis of systematic absences unambiguously identified the space group as *Ccca*. After initial refinement, it became apparent that the Mo-Mo unit has three-way disorder, and atoms Mo(2) and Mo(3) corresponding, respectively, to the second and the third orientations were located. These atoms were included in the

- (4) Crystal data for *mer*-MoCl₃(NH₂Cy)₃: monoclinic, *P*2₁/*c* (No. 14), *a* = 14.051(6) Å, *b* = 35.23(2) Å, *c* = 17.333(9) Å, β = 96.79(4)°, *V* = 8716(8) Å³, *Z* = 12, *T* = 20 °C, Rigaku AFC5R diffractometer equipped with a rotating Cu radiation source ($\lambda(\text{Cu K}\alpha) = 1.54184$ Å). We do not report the details of the crystal structure of **4a** because of poor refinement.
- (5) (a) Bino, A.; Cotton, F. A.; Fanwick, P. E. *Inorg. Chem.* **1979**, *18*, 3558. (b) Cotton, F. A.; Frenz, B. A.; Deganello, G.; Shaver, A. J. *Organomet. Chem.* **1973**, 227. (c) Cotton, F. A.; Dikarev, E. V.; Feng, X. *Inorg. Chim. Acta* **1995**, 237, 19.
- (6) *SHELXTL V.5*; Siemens Industrial Automation Inc.: Madison, WI, 1994.
- (7) Sheldrick, G. M. In *Crystallographic Computing 6*; Flack, H. D., Parkanyi, L., Simon, K., Eds.; Oxford University Press: Oxford, U.K., 1993; p 111.

Table 1. Crystallographic Data for Mo₂Cl₄(NH₂Prⁿ)₄ (**2**), MoCl₃(NH₂Prⁿ)₃·1/6THF (**2a**·1/6THF), Mo₂Cl₄(NH₂Bu^t)₄ (**3**), and Mo₂Cl₄(NH₂Cy)₄ (**4**)

	2	2a ·1/6THF	3	4
formula	Mo ₂ Cl ₄ N ₄ C ₁₂ H ₃₆	MoCl ₃ N ₃ O _{0.17} C _{9.67} H _{28.33}	Mo ₂ Cl ₄ N ₄ C ₁₆ H ₄₄	Mo ₂ Cl ₄ N ₄ C ₂₄ H ₅₂
fw	570.13	391.64	626.23	730.38
space group	<i>Ccca</i> (No. 68)	<i>P1</i> (No. 2)	<i>P2₁/c</i> (No. 14)	<i>P4₂2₁2</i> (No. 94)
<i>a</i> , Å	13.328(3)	12.370(2)	19.165(1)	15.556(4)
<i>b</i> , Å	26.639(5)	17.977(2)	20.858(1)	
<i>c</i> , Å	6.774(2)	25.498(6)	14.1400(8)	6.9368(8)
α, deg		95.32(1)		
β, deg		103.21(2)	99.002(5)	
γ, deg		103.48(1)		
<i>V</i> , Å ³	2405(1)	5304(2)	5582.8(5)	1678.6(6)
<i>Z</i>	4	12	8	2
ρ _{calcd} , g·cm ⁻³	1.575	1.471	1.490	1.445
μ, mm ⁻¹	1.489	1.183	1.290	1.084
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	-120	-100	-60	-60
transmission factors	0.8896–0.9983	0.9381–0.9999		
<i>R</i> 1, ^a <i>wR</i> 2 ^b [<i>I</i> > 2 σ(<i>I</i>)]	0.0316, 0.0732	0.0551, 0.1386	0.0451, 0.1024	0.0374, 0.0918
<i>R</i> 1, ^a <i>wR</i> 2 ^b (all data)	0.0705, 0.0839	0.0869, 0.1579	0.0582, 0.1183	0.0389, 0.0933

^a *R*1 = Σ||*F*_o| - |*F*_c||/Σ|*F*_o|. ^b *wR*2 = [Σ(*wF*_o² - *F*_c²)/Σ(*wF*_o²)]^{1/2}.

refinement, and their site occupancy factors (sof's) were allowed to vary against that of Mo(1) but constrained so that the sum of molybdenum atoms equaled 1. The sof's converged to final values of 0.698(2), 0.185(2), and 0.116(2). After anisotropic refinement of all non-hydrogen atoms, the residuals were *R* = 0.032 (for 560 reflections with *I* > 2σ(*I*) and *R* = 0.071 (for all 840 independent reflections). The final difference map was essentially featureless; the largest peak was 0.71 e Å⁻³.

mer-MoCl₃(NH₂Prⁿ)₃·1/6THF (2a**·1/6THF).** A red block of size 0.40 × 0.30 × 0.20 mm was used for diffraction study. The data were collected in the range 4° ≤ 2θ ≤ 46° with ω scan motion. The centrosymmetric space group *P1* was selected and confirmed by successful refinement. Some of the *n*-propyl groups appeared to be disordered on two sites. After anisotropic refinement of all non-disordered atoms, an interstitial molecule of tetrahydrofuran was located and included in calculations. The final residuals were *R* = 0.055 (for 10 628 reflections with *I* > 2σ(*I*)) and *R* = 0.087 (for all 14 699 data and 898/25 parameters/restraints). A final difference Fourier map contained several peaks (largest 1.69 e Å⁻³), all lying less than 1.0 Å from Mo atoms.

Mo₂Cl₄(NH₂Bu^t)₄ (3**).** A red plate with dimensions 0.50 × 0.40 × 0.10 mm grown from ether solution was selected and affixed to the tip of a quartz fiber with silicone grease. The diffraction data were collected on a Nonius FAST diffractometer at -60 °C. With 250 reflections (18° < 2θ < 42°), the unit cell was shown to be monoclinic primitive. Calculations in the space group *P2₁/c* revealed two crystallographically independent dimolybdenum molecules each having a second orientation of the Mo–Mo unit. The occupancies of the minor orientations were refined as 0.033(1) and 0.077(1), respectively. Also, two of four *tert*-butyl groups in the first molecule and three of four in the second molecule were found to be disordered. Final least-squares refinement of 492 parameters and 32 restraints led to *R* = 0.045 (for 8262 reflections with *I* > 2σ(*I*) and *R* = 0.058 (for all 9824 data). The highest peak in the final difference map was 1.10 e Å⁻³ located 1.05 Å from Mo(2).

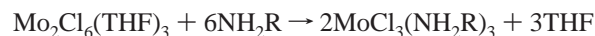
From the toluene/hexane and neat hexane solutions complex **3** crystallized as red needles. Their unit cell was shown to be primitive cubic, *a* = 17.984(2) Å, *V* = 5817(1) Å³, *Z* = 8. A total of 1283 unique data were collected in the range 4° < 2θ < 50° on a Nonius FAST diffractometer at -60 °C. Examination of the systematic absences narrowed the choice of space groups to *P4₃n* (No. 218) and *Pm3n* (No. 223). Refinement in the centrosymmetric space group (*Pm3n*) was unsuccessful since it did not provide a separation between ligand (Cl and N atoms) positions. Calculations in the non-centrosymmetric space group (*P4₃n*) revealed a highly disordered structure with two crystallographically independent dimolybdenum molecules each having threefold disorder. For this reason, the positions of Cl and N atoms are averaged for three orientations of the dimetal unit and have somewhat high thermal parameters. This in turn requires three-way disorder of tertiary carbon atoms of *tert*-butyl groups to keep Mo–N–C angles

intact for each Mo–Mo orientation. That disorder was actually found, with each tertiary carbon atom having its own set of three methyl groups. Final least-squares refinement of 109 parameters converged with *R* = 0.073. We will use in discussion the structural parameters for the non-disordered form of **3**, presuming them to be more reliable.

Mo₂Cl₄(NH₂Cy)₄ (4**).** A needle of dimensions 0.25 × 0.08 × 0.05 mm was mounted. Indexing based on 50 reflections in the range 18° < 2θ < 42° resulted in a primitive tetragonal cell, and cell parameters were further refined against 240 reflections. No absorption correction was made. Systematic absences in the data uniquely determined the space group to be *P4₂2₁2*. Only Mo, Cl, and N atoms were refined with anisotropic thermal parameters. A second orientation of the carbon atoms in the cyclohexyl ring was located, and its site occupancy factor was converged to 0.26(1). Final refinement of 67 parameters and 15 restraints resulted in *R* = 0.037 (for 1062 reflections with *I* > 2σ(*I*)) and *R* = 0.039 (for all data). The highest peak in the final difference map was 0.66 e Å⁻³. The absolute configuration of **4** was established by the method described by Flack (Flack *x* parameter = 0.0(2)).

Results and Discussion

Synthetic Aspects. Reactions of Mo₂Cl₆(THF)₃ with primary amines, NH₂R, at room temperature produce the reduced dimolybdenum species Mo₂Cl₄(NH₂R)₄ (*R* = Et (**1**), Prⁿ (**2**), Bu^t (**3**), Cy (**4**)). The yields of this process were very low (less than 25%) and did not increase even when the reaction mixture was refluxed. The main products were mononuclear molybdenum(III) complexes, MoCl₃(NH₂R)₃, as a result of simple substitution and metal–metal bond cleavage:



We have recently reported¹ that reaction between Mo₂Cl₆(THF)₃ and the secondary amine, NH₂Et₂, also gives the reduced dimolybdenum(II) complex Mo₂Cl₄(NH₂Et₂)₄. However, the yield in this case was about 50%, and other products, different Mo^{III} species, all having a Cl:Mo ratio >3, emerged when chloride ions, released upon substitution by amines, reacted with more starting material. Such parallel reactions also take place for primary amines, despite the fact that the concentration of Cl⁻ is relatively low.

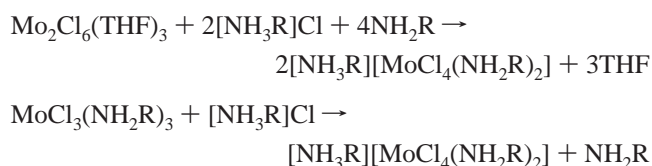


Table 2. Spectroscopic Data for the Complexes Mo₂Cl₄(NH₂R)₄ (R = Et (**1**), Prⁿ (**2**), Bu^t (**3**), Cy (**4**)) and Mo₂Cl₄(NHET₂)₄

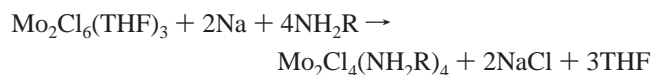
compd	IR (cm ⁻¹) ^a		vis (nm) δ-δ* trans	¹ H NMR			
	ν(N-H)	δ(N-H)		NH ₂	CH	CH ₂	CH ₃
Mo ₂ Cl ₄ (NH ₂ Et) ₄ (1)	3273 (vs) 3225 (vs)	1465 (m)	530 ^b	3.84 (t) ^d		2.76 (m)	1.23 (t)
Mo ₂ Cl ₄ (NH ₂ Pr ⁿ) ₄ (2)	3276 (vs) 3222 (vs)	1468 (m)	528 ^b	4.03 (t) ^e		2.62 (m) 1.03 (m)	0.59 (t)
Mo ₂ Cl ₄ (NH ₂ Bu ^t) ₄ (3)	3278 (w) 3193 (w)	1473 (w)	538 ^b	4.52 (s) ^e			1.08 (t)
Mo ₂ Cl ₄ (NH ₂ Cy) ₄ (4)	3287 (m) 3238 (m)	1448 (m)	530 ^b	4.41 (d) ^e	3.18 (m)	1.6-0.6	
Mo ₂ Cl ₄ (NHET ₂) ₄ ^f	3219 (m)	1460 (m)	534 ^c	4.50 (s) ^e		3.26 (s)	0.89 (s)

^a KBr pellets. ^b In THF. ^c In CH₂Cl₂. ^d In CDCl₃. ^e In C₆D₆. ^f Reference 1.

We were able to estimate the yields of the different products for the reactions with *tert*-butylamine and cyclohexylamine since it was possible to completely separate compounds based on their solubility. The MoCl₃(NH₂R)₃:Mo₂Cl₄(NH₂R)₄:[NH₃R][MoCl₄(NH₂R)₂] relative yields (based on the amount of Mo in Mo₂Cl₆(THF)₃) are 54:23:16 and 60:17:8 for R = Bu^t and Cy, respectively.

Despite the difference in reaction products for primary and secondary amines, the behavior of dimolybdenum(III) species in reactions of this type contrasts greatly with that of ditungsten(III) species. The latter are known to react with a variety of primary⁸ and secondary⁹ amines to produce only nonreduced compounds of the type W₂Cl₄(amide)₂(amine)₂ having both amido and amino groups. We have no evidence, so far, for the existence of molybdenum compounds of that type.

As in the case of NHET₂, the best results in the synthesis of reduced dimolybdenum(II) species with primary amine ligands were achieved by reduction of the starting material with sodium amalgam, in the presence of the appropriate amine.



The Mo₂Cl₄(NH₂R)₄ complexes (R = Et (**1**), Prⁿ (**2**), Bu^t (**3**), Cy (**4**)) can be isolated from the reaction mixture in nearly quantitative yield. The ethylamine compound **1** has limited solubility in all common solvents and therefore requires special treatment.

Properties of Mo₂Cl₄(NH₂R)₄ (R = Et (1**), Prⁿ (**2**), Bu^t (**3**), Cy (**4**)).** Complexes **2–4** are all readily soluble in dichloromethane, THF, toluene, and benzene. Complexes **3** and **4** can even be dissolved in diethyl ether or hexanes. However, compound **1** is only partially soluble in dichloromethane or chloroform and slightly soluble in THF. The solutions of these species are stable under nitrogen or argon atmosphere, and no sign of decomposition was observed when the solvents were evaporated. The behavior of an analogous complex with a secondary amine, Mo₂Cl₄(NHET₂)₄, in solution was found¹ to be completely different: it is stable only in the presence of free amine and undergoes partial decomposition (polymerization) when its solutions are under reduced pressure. In the solid state, compounds **1–4** are also more stable than the diethylamine derivative. These compounds are not very air sensitive even as powders and can be handled in the atmosphere for short periods of time.

The thermal stability of Mo₂Cl₄(NH₂Et)₄ (**1**) was studied under the same conditions used for Mo₂Cl₄(NHET₂)₄ in order to compare the data. Although the loss of the amine for Mo₂Cl₄(NHET₂)₄ starts at about 65 °C, it is not significant until 90 °C. However, for compound **1** this process starts only at 135 °C. That difference is substantial, especially if the boiling points of both amines are considered (55 °C for NHET₂ and 16.6 °C for NH₂Et). The thermogravimetric weight loss curve for complex **1** presents a continuously decreasing line between 135 °C (the beginning of the weight loss) and 325 °C (when the line becomes flat and the weight loss corresponds to the loss of the four amines). There are no clear steps in the overall process as was observed for the diethylamine compound.

The infrared spectra of the complexes **1–4** (Table 2) exhibit two absorptions due to N-H stretching between 3193 and 3287 cm⁻¹, and one absorption for N-H bending between 1473 and 1448 cm⁻¹. Corresponding bands appear at 3219 and 1460 cm⁻¹, respectively, for Mo₂Cl₄(NHET₂)₄.¹ The electronic spectra of the complexes with primary amines show the maximum of the δ-δ* transition absorption band between 538 and 528 nm (Table 2).

The ¹H NMR spectra of complexes **1–4** display well-defined signals (Figure 1), instead of the very broad signals which characterize the Mo₂Cl₄(NHET₂)₄ spectrum because of the exchange in solution between the coordinated amines and the free amine liberated in the decomposition process. No free amine was detected in the spectra of complexes **1–4**. The signals of the hydrogen nuclei of the NH₂ group for compounds **1** and **2** are triplets. Although they are broader than the rest of the signals in the spectrum, the coupling with the nearest hydrogen nuclei of the CH₂ groups is observed in both cases. For complex **3**, the nearest hydrogen atoms are farther away and no coupling between hydrogen nuclei of NH₂ and CH₃ groups is resolved. For compound **4**, the signal of the NH₂ group is a doublet, because the closest carbon atom is bonded to only one hydrogen atom.

Molecular Structures. Crystal structures of Mo₂Cl₄(NH₂R)₄ (R = Prⁿ (**2**), Bu^t (**3**), Cy (**4**)) are very similar. Perspective drawings of the molecules **2–4** are depicted in Figures 2–4, respectively. The central portions of each structure consisting of the non-centrosymmetric Mo₂Cl₄N₄ core are the same, and each has D_{2d} symmetry. The Mo-Mo bond distances in all of them (**2**, 2.118(2) Å; **3**, 2.1322(6) Å; **4**, 2.117(1) Å) fall within the range of the bond distances established for the Mo-Mo quadruple bond with a σ²π⁴δ² configuration.¹⁰ Each Mo atom in the molecules is approximately square planar with the two nitrogen atoms of primary amines in a trans arrangement in each

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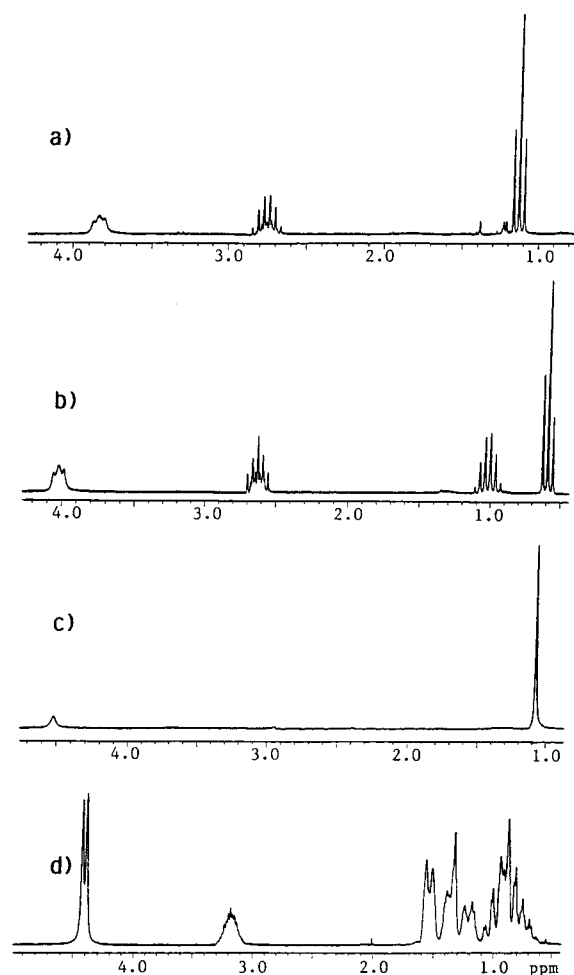


Figure 1. ^1H NMR spectra of (a) $\text{Mo}_2\text{Cl}_4(\text{NH}_2\text{Et})_4$ (**1**) in CDCl_3 , (b) $\text{Mo}_2\text{Cl}_4(\text{NH}_2\text{Pr}^n)_4$ (**2**) in C_6D_6 , (c) $\text{Mo}_2\text{Cl}_4(\text{NH}_2\text{Bu})_4$ (**3**) in C_6D_6 , and (d) $\text{Mo}_2\text{Cl}_4(\text{NH}_2\text{Cy})_4$ (**4**) in C_6D_6 , at room temperature.

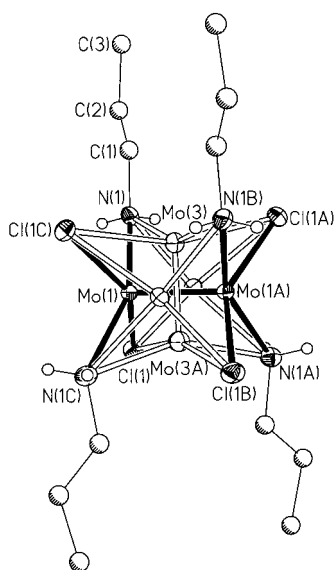


Figure 2. Perspective drawing of $\text{Mo}_2\text{Cl}_4(\text{NH}_2\text{Pr}^n)_4$ (**2**). Atoms are represented by thermal ellipsoids at the 40% probability level. All three orientations of the dimolybdenum unit are depicted. Carbon and amine hydrogen atoms are shown as spheres of arbitrary radii.

MoCl_2N_2 fragment. The molecular dimensions for the three complexes **2–4** (Tables 3 and 4) are not significantly different from those of the recently determined¹ structure of the analogous complex $\text{Mo}_2\text{Cl}_4(\text{NH}_2\text{Et})_4$, except for the Mo–N distances,

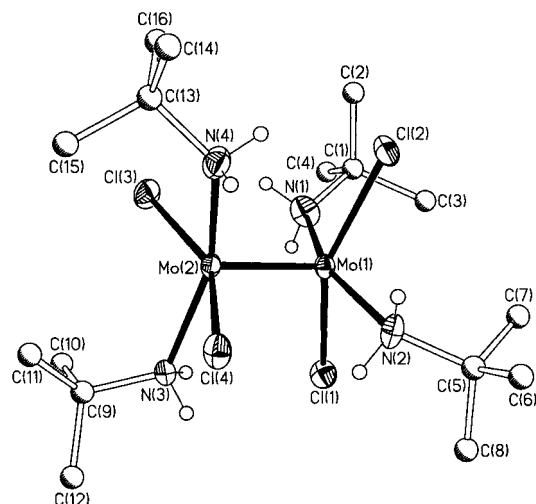


Figure 3. Perspective drawing of one crystallographically independent molecule of $\text{Mo}_2\text{Cl}_4(\text{NH}_2\text{Bu})_4$ (**3**). Atoms are represented by thermal ellipsoids at the 40% probability level. Only the major orientation of the dimolybdenum unit is depicted. Hydrogen atoms of *tert*-butyl groups are omitted. Carbon and amine hydrogen atoms are shown as spheres of arbitrary radii.

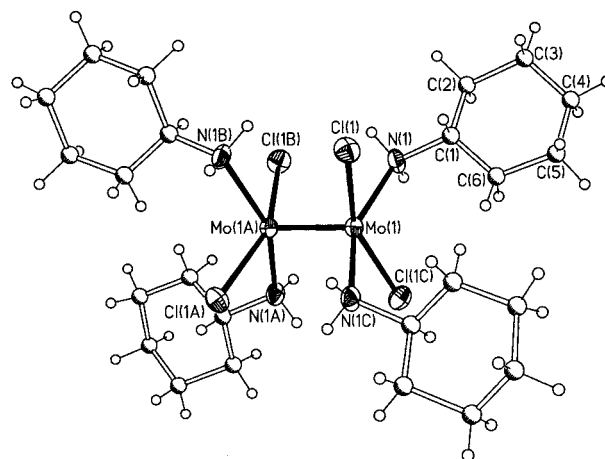


Figure 4. Perspective drawing of $\text{Mo}_2\text{Cl}_4(\text{NH}_2\text{Cy})_4$ (**4**). Atoms are represented by thermal ellipsoids at the 40% probability level. Only the major orientation of cyclohexyl rings is displayed. Carbon and hydrogen atoms are shown as spheres of arbitrary radii.

Table 3. Selected Bond Distances (Å), Angles (deg), and Torsion Angles (deg) for $\text{Mo}_2\text{Cl}_4(\text{NH}_2\text{Pr}^n)_4$ (**2**) and $\text{Mo}_2\text{Cl}_4(\text{NH}_2\text{Cy})_4$ (**4**)

	2	4
Mo(1)–Mo(1A)	2.118(2)	2.117(1)
Mo(1)–N(1)	2.220(4)	2.239(5)
Mo(1)–Cl(1)	2.404(1)	2.432(2)
N(1)–Mo(1)–N(1B)	155.3(3)	154.3(3)
Cl(1)–Mo(1)–Cl(1B)	148.64(8)	156.5(1)
N(1)–Mo(1)–Cl(1)	82.8(1)	87.3(1)
N(1)–Mo(1)–Cl(1B)	90.6(1)	87.5(1)
Mo(1A)–Mo(1)–N(1)	102.3(2)	102.8(1)
Mo(1A)–Mo(1)–Cl(1)	105.68(4)	101.77(5)
N–Mo–Mo–Cl	7.7(1)	2.8(2)

which are more than 0.03 Å longer in the case of the compound with secondary amine ligands.

One interesting structural feature of molecules **2–4**, which reflects an effect of packing forces, is an orientation of nitrogen-connected atoms (one carbon and two hydrogens) relative to the Mo–Mo bond. This orientation of substituents on the amine ligands can be characterized by the torsion angles Mo–Mo–N–C and Mo–Mo–N–H. The difference among the title

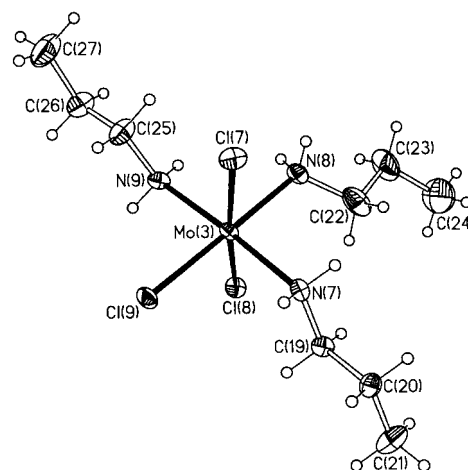
Table 4. Averaged Bond Distances (Å), Angles (deg), and Torsion Angles (deg) for Two Crystallographically Independent Molecules $\text{Mo}_2\text{Cl}_4(\text{NH}_2\text{Bu}^n)_4$ (**3**)

Mo–Mo	2.1309(6)	2.1335(6)
Mo–N	2.248(4)	2.254(4)
Mo–Cl	2.439(1)	2.431(1)
N–Mo–N	158.3(2)	160.3(2)
Cl–Mo–Cl	153.81(5)	152.31(5)
N–Mo–Cl	82.8(1), 92.4(1)	84.1(1), 91.2(1)
Mo–Mo–N	100.9(1)	99.9(1)
Mo–Mo–Cl	103.08(4)	103.84(4)
N–Mo–Mo–Cl	3.9(1)	2.9(1)

structures is that while in the $\text{Mo}_2\text{Cl}_4(\text{NH}_2\text{Pr}^n)_4$ (**2**) molecule the *n*-propyl group is located “perpendicular” to the metal–metal axis ($\angle\text{Mo–Mo–N–C}$ is 74°), the *tert*-butyl (in **3**) and cyclohexyl (in **4**) groups are directed “parallel” to the Mo–Mo vector ($\angle\text{Mo–Mo–N–C}$ vary in the range $144\text{--}177^\circ$). Therefore, in the latter two cases one of the two amine hydrogen atoms is located more or less above the metal–metal axis, allowing hydrogen bonding with the chlorine atom across the dinuclear molecule. Indeed, in the structure of $\text{Mo}_2\text{Cl}_4(\text{NH}_2\text{Bu}^n)_4$ (**3**), where the torsion angles Mo–Mo–N–H are in the range $20\text{--}27^\circ$, there are two strong N–H \cdots Cl bonds per molecule, each having an H \cdots Cl separation of about 2.4 Å with corresponding N–H–Cl angles of $135\text{--}142^\circ$. At the other extreme, one of the Mo–Mo–N–H angles in propylamine complex is 56° , providing a long N–H \cdots Cl contact of 2.95 Å and an acute N–H–Cl angle of 107° . Another hydrogen atom in this structure is directed away from the dimetal unit (Mo–Mo–N–H angle of 160°), giving an intramolecular hydrogen bonding with the N–H \cdots Cl parameters being 2.67 Å and 158° .

We would like to note that there are just a few known examples of molybdenum compounds with primary amine ligands NH_2R (R = Me,¹¹ Bu,¹² Ph¹³). They include different oxidation states for Mo atoms from +2 to +6 and display Mo– NH_2R bonds in the range 2.19–2.38 Å.

The compound $\text{MoCl}_3(\text{NH}_2\text{Pr}^n)_3 \cdot \frac{1}{6}\text{THF}$ (**2a** $\cdot\frac{1}{6}\text{THF}$) crystallizes in the triclinic space group *P*1 with the asymmetric unit composed of six molecules of the mononuclear complex (Figure 5) and one molecule of THF. The propylamine ligands on each octahedrally-coordinated metal center are in a meridional conformation, and Mo–N and Mo–Cl distances are in the ranges 2.198(6)–2.232(6) and 2.400(2)–2.439(2) Å, respectively. The angles at the Mo atom vary in the ranges $83.5(2)\text{--}96.4(2)^\circ$ and $172.15(7)\text{--}179.0(2)^\circ$. The octahedral Mo^{III} complex is one of the well-established class of MoCl_3L_3 compounds (where L is a neutral donor) known to include both meridional (L = py,^{14a} pic,^{14b} THF,^{14c} THT,^{14d} OPMe₃,^{14e} PMe₂Ph^{14f}) and facial (L = OC(NH₂)₂,^{14g} SC(NH₂)₂,^{14h} CH₃CN,¹⁴ⁱ 2-SC₅H₂-NH-3,6-(SiMe₂Bu)₂)^{14j} isomers.

**Figure 5.** Perspective drawing of one crystallographically independent molecule of *mer*- $\text{MoCl}_3(\text{NH}_2\text{Pr}^n)_3$ in **2a** $\cdot\frac{1}{6}\text{THF}$. Atoms are represented by thermal ellipsoids at the 40% probability level. Hydrogen atoms are shown as spheres of arbitrary radius.

Conclusions

It has been shown already that the newly-synthesized dimolybdenum complex $\text{Mo}_2\text{Cl}_4(\text{NHEt}_2)_4$ can serve effectively as a starting material for exploring the chemistry of the Mo_2^{4+} core. However, this compound is hard to store in the solid state and it is rather unstable in solution, losing amine ligands spontaneously when kept in the absence of free amine. As a result of our quest for a more amenable material, the quadruply-bonded dimolybdenum molecules of the general type $\text{Mo}_2\text{Cl}_4(\text{NH}_2\text{R})_4$, where NH_2R is a primary amine (R = Et (**1**), Prⁿ (**2**), Buⁿ (**3**), Cy (**4**)), are now accessible by the reduction of an easily available Mo^{III} species. These complexes have greater stability than those with secondary amine ligands: they are stable in solution without excess amine present, and they have higher decomposition temperatures as solids. These properties make them more attractive for use in the synthesis of new dimolybdenum(II) compounds.

On the basis of the relative stability of the complexes $\text{Mo}_2\text{Cl}_4\text{L}_4$ with primary and secondary amines, one can assume that tertiary amine compounds would be the least stable. Indeed, we were unable so far to isolate any of those species on the same reaction route. Further work, including the study of aromatic amines, is currently underway.

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Supporting Information Available: Four 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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