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Divalent Molybdenum Complexes of the Dipyrrolide Ligand System. Isolation of a Mo_2 Unit with a 45° Twist Angle

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The preparation of divalent Mo complexes of dipyrrolide dianions was carried out by reacting Mo_2(acetate)$_4$ with the dipotassium salts of $Ph_2C(2\text{-}C_4H_3NH)_2$ and 2-[1,1-bis(1*H*-pyrrol-2-yl)ethyl]pyridine. The two reactions respectively afforded the diamagnetic $\{[Ph_2C(C_4H_3N)_2]_2Mo_2(OAc)_2[K(THF)_3][K(THF)]\}\cdot THF$ (**1**) and $\{[(2\text{-}C_5H_4N)(CH_3)C(2\text{-}C_4H_3N)_2]\text{-}Mo(OAc)[K(THF)]\}_2\cdot THF$ (**2**). Both compounds retained two acetate units in the dimetallic structure. Conversely, the reaction of $Me_8Mo_2Li_4(THF)_4$ with $Et_2C(2\text{-}C_4H_3NH)_2$ afforded the paramagnetic dimer $\{[Et_2C(C_4H_3N)_2]_4Mo_2Li_2\}\text{-}\{Li(THF)_4\}_2\cdot 0.5THF$ (**3**). The paramagnetism is most likely caused by the 45° rotation of the two Mo(dipyrrolide) units with respect to each other and which, in turn, is caused by the presence of two lithium cations in the molecular structure.

Introduction

Since the historical discovery of the existence of quadruply bonded divalent dimolybdenum complexes,[1] several important advances have been made toward both the preparation and the understanding of this large family of complexes.[2] Today, it is common knowledge that Mo−Mo quadruple bonds are robust and capable of holding dinuclear frames together. The $\sigma^2\pi^4\delta^2$ ground state has been successfully calculated and interpreted from both the experimental and theoretical point of view.[2−5]

The general robustness of the Mo−Mo bonds can be exploited for a variety of applications, including the assembly of supramolecular structures and formation of oligonuclear or polymeric structures.[6] On the other hand, it has been recently recognized that the stability introduced by the M−M multiple bond could be an impediment toward further reactivity.[7] In fact, the chemical behavior reported so far for divalent Mo clusters is not what one would expect for a highly reduced second-row metal. Nonetheless, the expectations for the high reactivity of mononuclear midvalent Mo species are substantiated by the unique reactivity of trivalent and mononuclear Mo derivatives of bulky amides with dinitrogen.[8] Thus, a significant development of the potential of Mo clusters for molecular activation purposes may be anticipated if Mo−Mo multiple bond formation could be somehow prevented without the use of strong ligands such as CO, Cp, or phosphines. A possible strategy with this respect might be that of enforcing some degree of rotation along the Mo−Mo bond with consequent reduction of the

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(1) (a) Lawton, D.; Mason, R. *J. Am. Chem. Soc.* **1965**, *87*, 921. (b) Cotton, F. A.; Mester, Z. C.; Webb, T. R. *Acta Crystallogr.* **1974**, *B30*, 2768.

(2) (a) Cotton, F. A.; Walton, R. A. *Multiple bonds between metal atoms*, 2nd ed.; Clarendon Press: Oxford, U.K., 1993. (b) Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry*, 6th ed.; Wiley: New York, 1999. (c) Cotton, F. A.; Nocera, D. G. *Acc. Chem. Res.* **2000**, *33*, 483.

(3) See for example: (a) Chisholm, M. H. *J. Organomet. Chem.* **2002**, *641*, 15 and references cited therein. (b) Nishino, M.; Yoshioka, Y.; Yamaguchi, K.; Mashima, K.; Tani, K.; Nakamura, A. *Bull Chem Soc. Jpn.* **1998**, *71*, 99.

(4) Lichtenberger, D. L.; Ray, C. D.; Stepniak, F.; Chen, Y.; Weaver, J. H. *J. Am. Chem. Soc.* **1992**, *114*, 10492.

(5) Ceylan, V. K. *Transition Met. Chem.* **1998**, *23*, 191.

(6) See for example: (a) Bursten, B. E.; Chisholm, M. H.; Clark, R. J. H.; Firth, S.; Hadad, C. M.; Wilson, P. J.; Woodward, P. M.; Zalenski, J. M. *J. Am. Chem. Soc.* **2002**, *124*, 12244 and references cited therein. (b) Cotton, F. A.; Donahue, J. P.; Lin, C.; Murillo, C. A. Rockwell, J. *Acta Crystallogr.* **2002**, *E58*, m298. (c) Cotton, F. A.; Daniels, L. M.; Donhaue, J. P. ; Liu, C. Y.; Murillo, C. A. *Inorg. Chem.* **2002**, *41*, 1354. (d) Cotton, F. A.; Lin, C.; Murillo, C. A. *Inorg. Chem.* **2001**, *40*, 6413. (e) Chisholm, M. H. *Abstracts of Papers*, 222nd National Meeting of the American Chemical Society; American Chemical Society: Washington, DC, 2001; pp 26−30. (f) Cotton, F. A.; Daniels, L. M.; Lin, C.; Murillo, C. A. *Inorg. Chem. Commun.* **2001**, *4*, 130. (g) Suen, M. C.; Tseng, G. W.; Chen. J. D.; Keng, T. C.; Wang, J. C. *J. Chem. Soc., Chem. Commun.* **1999**, *13*, 1185. (h) Cotton, F. A.; Daniels, L. M.; Guirnet, I.; Henning, R. W.; Jordan, G. T.; Lin, C.; Murillo, C. A.; Schultz, A. J. *J. Am. Chem. Soc.* **1998**, *120*, 12531.

(7) Floriani, C.; Solari, E.; Franceschi, F.; Scopelliti, R.; Belanzoni, P.; Rosi, M. *Chem.—Eur. J.* **2001**, *7*, 3052.

(8) (a) Laplaza, C. E.; Cummins, C. C. *Science* **1995**, *268*, 861. (b) Yandulov, D. V.; Schrock, R. R. *Science* **2003**, *301*, 76.

10.1021/ic0350739 CCC: $27.50

formal Mo−Mo bond order. Although the weakening of the π and δ bonds is not expected to involve large amounts of energy,[2c] still it could make these stable clusters more susceptible to a radical type of attack.

The dipyrrolide dianion ligand system has displayed a unique versatility in assembling both large cyclic[9] or linear clusters.[10] However, the σ- or π-bonding mode or the combination of both, as usually adopted by these dianions in aggregating polynuclear structures, has so far never shown ability to support the formation of M−M multiple bonds. In addition, the resiliency of dipyrrolide dianions toward strongly reducing agents also makes this family of ligands promising for exploring the chemistry of highly reactive low-valent metals. Thus, we became interested in probing how dipyrrolide anions may stabilize the lower oxidation states of Mo and eventually favor or disfavor formation of Mo−Mo multiple bonds. It should be reiterated that these ligands so far have shown a great tendency to intimately bound alkali metal cations whose nature in turn affects the nuclearity and arrangement of cluster structures. In this first report, we describe our preliminary findings as well as the characterization of a paramagnetic divalent Mo_2 unit with a torsion angle of 45°.

Experimental Section

All operations were performed under inert atmosphere by using standard Schlenk type techniques or inside a drybox. $(CH_3)_8Mo_2Li_4(OEt_2)_4$,[11] $Mo_2(OAc)_4$,[2] diethyldipyrrolylmethane,[12] and diphenyldipyrrolylmethane[9,10] were prepared according to published procedures. Samples for magnetic susceptibility measurements at variable temperatures were preweighed inside a drybox equipped with an analytical balance and flame sealed into calibrated 5 mm o.d. quartz tubes. Magnetic measurements were carried out using a Quantum Design MPMS5S SQUID magnetometer at 0.1 T, in the temperature range 2−300 K. The accurate sample mass was determined by difference by breaking the tube after data collection. Background data on the cleaned, empty tube were obtained under identical experimental conditions. **3** was weighed into a standard gelcap and sealed in a glass tube in the drybox for shipment. The gelcap was sealed with Kapton tape on breaking the glass tube and quickly loaded into the SQUID magnetometer. Background corrections for the gelcap were included in the magnetic calculations. Standard corrections for underlying diamagnetism were applied to data.[13] Elemental analyses were carried out with a Perkin-Elmer 2400 CHN analyzer. Data for X-ray crystal structure determinations were obtained with a Bruker diffractometer equipped with a Smart CCD area detector. NMR spectra were recorded with a Bruker AMX-500 instrument.

Preparation of 2-[1,1-Bis(1*H*-pyrrol-2-yl)ethyl]pyridine. A solution of acetylpyridine (29.8 g, 0.24 mol) in ethanol (250 mL) was treated with pyrrole (67.1 g, 1.0 mol). After the addition of catalytic amount of CH_3SO_3H (5 mL), the mixture was refluxed for 3 days during which the color of the mixture turned dark-red. The solvent was removed in vacuo, and the residual viscous solid was redissolved in $CHCl_3$ and filtered through a column of silica gel obtaining a colorless filtrate. The solvent was removed in vacuo and the residue washed with several portions of ether affording a colorless solid. Recrystallization from MeOH afforded analytically pure product (15.2 g, 0.064 mol, 26%). Anal. Calcd (found) for $C_{15}H_{15}N_3$: C, 75.92 (75.79); H, 6.37 (6.31); N, 17.71 (17.67). ^1H NMR ($CDCl_3$, 500 MHz, 25 °C): δ 9.05 (N−H, 2H), 8.62 (d, C−H pyridine, 1H), 7.59 (pseudo-q, C−H pyridine, 1H), 7.16 (m, C−H pyridine, 2H), 6.73 (m, C−H pyrrolyl, 2H), 6.16 (m, C−H pyrrolyl, 2H), 5.94 (m, C−H pyrrolyl, 2H), 2.08 (s, CH_3, 3H). MS: $m/e^+ =$ 237.

Preparation of $\{[Ph_2C(2\text{-}C_4H_3N)_2]_2Mo_2(OAc)_2[K(THF)_3][K(THF)]\}\cdot THF$ (1). Solid diphenyldipyrrolmethane (0.14 g, 0.46 mmol) was added to a stirred suspension of KH (0.037 g, 0.92 mmol) in THF (10 mL). A vigorous reaction with gas evolution took place. When the reaction terminated, solid $Mo_2(OAc)_4$ (0.10 g, 0.23 mmol) was added immediately turning the color to purple. Stirring was continued overnight, after which the reaction mixture was centrifuged to eliminate a small amount of white solids. The surnatant was concentrated to small volume (5 mL) and allowed to stand −35 °C for 1 week upon which red crystals of **1** separated (0.20 g, 0.15 mmol, 65% yield). Anal. Calcd (found) for $C_{66}H_{78}N_4O_9K_2Mo_2$: C, 59.09 (59.00); H, 5.86 (5.81); N, 4.18 (4.14). ^1H NMR (THF-d_8, 500 MHz, 25 °C): δ 7.36 (s, C−H pyrrolyl, 4H), 7.08 (s, C−H phenyl, 4H), 6.99 (m, C−H phenyl, 6H), 6.83 (m, C−H phenyl. 6H), 6.44 (m, C−H phenyl, 4H), 5.99 (m, C−H pyrr, 4H), 5.31 (m, C−H pyrr, 4H), 3.58 (overlapping m, THF, 36H), 2.68 (s, CH_3 acetate, 6H), 1.73 (overlapping m, THF, 36H). ^{13}C NMR (THF-d_8, 123.72 MHz, 25 °C): δ 179.17, 151.00, 149.89, 142.95, 57.43 (quaternary), 128.75, 127.75, 125.08, 124.48, 122.93, 122.70 (C−H phenyl), 128.87, 108.36, 105.47 (C−H pyrr), 21.21 (Me acetate), 64.95 and 22.87 (THF).

Preparation of $\{[(2\text{-}C_5H_4N)(CH_3)C(2\text{-}C_4H_3N)_2]Mo(OAc)[K(THF)]\}_2\cdot THF$ (2). Solid methylpyridyldipyrromethane (0.56 g, 2.34 mmol) was added to a stirred suspension of KH (0.19 g, 4.68 mmol) in THF (50 mL). A vigorous reaction took place, after which solid $Mo_2(OAc)_4$ (0.50 g, 1.17 mmol) was added. The color of the reaction mixture immediately turned purple. Stirring was continued overnight, after which the reaction mixture was centrifuged to eliminate a small amount of white solid. The clear solution was concentrated to small volume (25 mL) and allowed to stand at −35 °C for 1 week upon which red crystals of **2** separated (0.75 g, 0.70 mmol, 60% yield). Anal. Calcd (found) for $C_{46}H_{56}K_2Mo_2N_6O_7$: C, 51.39 (51.31); H, 5.25 (5.19); N, 7.82 (7.77). The very poor solubility in the most common deuterated solvents prevented NMR characterization.

Preparation of $\{[Et_2C(2\text{-}C_4H_3N)_2]_4Mo_2Li_2\}\{Li(THF)_4\}_2\cdot 0.5THF$ (3). Solid diethyldipyrrolmethane (0.64 g, 3.16 mmol) was added to a stirred solution of $(CH_3)_8Mo_2Li_4(Et_2O)_4$ (0.50 g, 0.79 mmol) in THF (40 mL). The color of the reaction mixture instantly changed from red to dark-brown. After overnight stirring, the mixture was centrifuged to eliminate a small amount of insoluble material. The surnatant was concentrated to small volume (20 mL) and layered with hexane (20 mL). Dark-brown crystal of **3** separated upon allowing the solution to stand at room temperature for 1 week (0.61 g, 0.37 mmol, 47% yield). Anal. Calcd (found) for $C_{86}H_{132}N_8O_{8.5}Li_4Mo_2$: C, 63.23 (63.16); H, 8.14 (8.09); N, 6.86 (6.76).

X-ray Crystallography. Compounds **1**−**3** consistently yielded crystals that diffracted weakly, and the results presented are the

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(9) Dube, T.; Conoci, S.; Gambarotta, S.; Yap, G. P. A.; Vasapollo, G. *Angew. Chem., Int. Ed.* **1999**, *38*, 3657.

(10) Ganesan, M.; Lalonde, M. P.; Gambarotta, S.; Yap, G. P. A. *Organometallics* **2001**, *20*, 2443.

(11) Cotton, F. A.; Troup, J. M.; Webb, T. R.; Williamson, T. H.; Wilkinson, G. *J. Am. Chem. Soc.* **1974**, *96*, 3824.

(12) Berube, C.; Yazdanbakhsh, Gambarotta, S,; Yap, G. P. A. *Organometallics*, in press.

(13) (a) Mabbs, M. B.; Machin, D. *Magnetism and Transition Metal Complexes*; Chapman and Hall: London, 1973. (b) Foese, G.; Gorter, C. J.; Smits, L. J. *Selected Constants for Dimagnetism and Paramagnetism*; Masson: Paris, 1957.

Table 1. Crystal Data and Structure Analysis Results

	1	**2**	**3**
formula	$C_{86}H_{132}Li_4Mo_2N_8O_{8.5}$	$C_{66}H_{78}K_2Mo_2N_4O_9$	$C_{46}H_{56}K_2Mo_2N_6O_7$
M_r	1633.64	1341.40	1075.38
cryst system	triclinic	monoclinic	triclinic
space group	$P\bar{1}$ (No. 2)	$P2_1$ (No. 4)	$P\bar{1}$ (No. 2)
Z	2	2	2 ($Z' = 6$)
a (Å)	12.835(2)	10.9979(17)	17.814(11)
b (Å)	14.900(3)	19.719(3)	19.222(12)
c (Å)	24.924(5)	16.250(3)	24.277(15)
α (deg)	93.266(3)		83.852(11)
β (deg)	93.179(3)	96.394(3)	88.904(11)
γ (deg)	108.017(3)		73.392(11)
V (Å^3)	4511.9(14)	3502.2(9)	7919(8)
radiation (Mo Kα)	0.710 73	0.710 73	0.710 73
T (K)	223(2)	203(2)	203(2)
D_{calcd} (g cm^{-3})	1.202	1.272	1.353
μ_{calcd} (cm^{-1})	3.33	5.30	6.83
F_{000}	1736	1392	3312
reflcns collcd/unique	22 828/12 359	24 110/11 649	44 479/25 422
R(int)	0.0499	0.0468	0.0636
params rfnd	1027	793	1477
R, $R_w{}^2$ [a]	0.0701, 0.2065	0.0635, 0.1532	0.0788, 0.2305
GoF	1.120	1.077	1.041

[a] $R = \sum F_o - F_c/\sum F_o$; $R_w = [(\sum(F_o - F_c)^2/\sum_w F_o^2)]^{1/2}$.

best of several trials. The data crystals were selected, mounted on a thin glass fibers using paraffin oil, and cooled to the data collection temperature for **1**−**3**. Data were collected on a Bruker AXS SMART 1k CCD diffractometer using 0.3° ω-scans at 0, 90, and 180° in ϕ. Initial unit-cell parameters were determined from 60 data frames collected at different sections of the Ewald sphere. Semiempirical absorption corrections based on equivalent reflections were applied.[15]

Systematic absences in the diffraction data sets and unit-cell parameters were consistent with $P\bar{1}$ (No. 2) for **1** and **3** and $P2_1$ (No. 4) for **2**. The structures were solved by direct methods, completed with difference Fourier syntheses, and refined with full-matrix least-squares procedures based on F^2.

One cocrystallized THF solvent molecule with 50% occupancy was located in the asymmetric unit in the case of **3**. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were treated as idealized contributions. All scattering factors are contained in several versions of the SHELXTL program library with the latest used version being v.6.12 (Sheldrick, G. M. *SHELXTL*; Bruker AXS: Madison, WI, 2001). Crystallographic data and relevant bond distances and angles are reported in Tables 1 and 2.

Description of the Crystal Structures. Compound 1. The structure (Figure 1) consists of two molybdenum atoms linked by two acetates that adopted the usual three-center chelating geometry [Mo(1)−O(1) = 2.144(6) Å, Mo(1)−O(3) = 2.151(6) Å, torsion angle O(1)−Mo(1)−Mo(2)−O(2) = 3.9(2)°]. Each Mo atom bears one dipyrrolide dianion which acts as a regular chelating and bidentate ligand with the two N atoms σ-bonded to the metal [Mo(1)−N(1) = 2.148(6) Å, Mo(1)−N(2) = 2.161(7) Å]. Thus, the coordination geometry around each Mo atom can be regarded as distorted square pyramidal considering two O and two N atoms of the ligand system defining the basal plane [O(1)−Mo(1)−O(3) = 88.4(2)°, O(1)−Mo(1)−N(2) = 153.9(2)°, O(1)−Mo(1)−N(1) = 90.2(2)°, O(3)−Mo(1)−N(1) = 160.7(2)°, O(3)−Mo(1)−N(2) = 87.3(2)°, N(1)−Mo(1)−N(2) = 85.6(2)°] and the second Mo atom as occupying the axial position [Mo(2)−Mo(1)−O(1) = 92.31(16)°, Mo(2)−Mo(1)−O(3) = 90.52(16)°, Mo(2)−Mo(1)−N(1) = 108.73(18)°, Mo(2)−Mo(1)−N(2) = 113.45(16)°]. Two potassium atoms also are part of the structure showing completely different coordination environments. The first is placed at the exterior of the molecule and appears to be σ-bonded to one O atom of one of the two acetates [K(1)−O(1) = 2.964(6) Å] and π-bonded to one pyrrolyl ring [K(1)−C(1) = 2.992(8) Å, K(1)−C(2) = 3.210(9) Å, K(1)−C(3) = 3.452(9) Å, K(1)−C(4) = 3.394(8) Å, K(1)−N(1) = 3.103(7) Å]. Three molecules of THF complete its coordination sphere. The second potassium atom is π-bonded to two pyrrolide rings from two different ligands [K(2)−N(2) = 2.915(7) Å, K(2)−C(6) = 3.171(8) Å, K(2)−C(8) = 3.116(8) Å, K(2)−C(9) = 2.877(8) Å], but it is also π-coordinated to one phenyl ring of one ligand [K(2)−C(37) = 3.106(9) Å, K(2)−C(41) = 3.225(8) Å]. One molecule of THF completes the pseudotetrahedral coordination sphere.

Compound 2. The crystal structure (Figure 2) showed that the Mo_2 unit still retained two acetate groups [Mo(1)−O(2) = 2.109(7) Å, Mo(1)−O(3) = 2.129(7) Å], while two dipyrrolide anions [Mo(1)−N(1) = 2.143(8) Å, Mo(1)−N(2) = 2.156(8) Å] and two potassium atoms each bonded to one molecule of THF to complete the structure. The two acetate groups are placed cis to each other similarly to **1** and adopted the usual three-center chelating geometry [O(2)−Mo(1)−O(3) = 86.7(3)°, O(1)−Mo(2)−O(4) = 86.4(3)°]. The coordination geometry around each Mo is better described as distorted square pyramidal and is defined by the two oxygen atoms from two acetate groups and two N atoms from two pyrrolide rings of one dipyrrolide anion [N(1)−Mo(1)−N(2) = 85.5(3)°, N(1)−Mo(1)−O(3) = 88.9(3)°, N(1)−Mo(1)−O(2) = 157.1(3)°, N(2)−Mo(1)−O(2) = 90.1(3)°, N(2)−Mo(1)−O(3) = 157.6(3)°, O(2)−Mo(1)−O(3) = 86.7(3)°]. The second Mo atom occupies the axial position [Mo(2)−Mo(1)−N(1) = 111.4(2)°, Mo(2)−Mo(1)−N(2) = 111.0(2)°, Mo(2)−Mo(1)−O(2) = 91.2(2)°, Mo(2)−Mo(1)−

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(14) (a) ADF2002.03, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, http://www.scm.com. Baerends, E. J.; Ros, P. *Chem Phys.* **1975**, *8*, 412. (b) Fonseca Guerra, C.; Snijders, J. G.; Velde, G. T.; Baerends, E. J. *Theor. Chem. Acc.* **1998**, *99*, 391. (c) te Velde, G.; Bickelhaupt, F. M.; van Gisbergen, S. J. A.; Fonseca Guerra, C.; Baerends, E. J.; Snijders, J. G.; Ziegler, T. *J. Comput. Chem.* **2001**, *22*, 931. (d) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098. (e) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822. (f) Snijdler, J. G.; Baerends, E. J.; Vernooijs, P. *At. Data Nucl. Data Tables* **1982**, *26*, 483. (g) Baerends, E. J.; Ellis, D. E.; Ros, P. *Chem. Phys.* **1973**, *2*, 41.

(15) Blessing, R. *Acta Crystallogr.* **1995**, *A51*, 33.

Table 2. Selected Bond Distances (Å) and Angles (deg)

1	**2**	**3**
Mo(1)−Mo(2) = 2.1561(9)	Mo(1)−Mo(2) = 2.1475(14)	Mo(1)−Mo(2) = 2.2464(9)
Mo(1)−O(1) = 2.146(6)	Mo(1)−O(2) = 2.109(7)	Mo(1)−N(1) = 2.2175(7)
Mo(1)−O(3) = 2.151(6)	Mo(1)−O(3) = 2.129(7)	Mo(1)−N(2) = 2.232(6)
Mo(1)−N(1) = 2.148(6)	Mo(1)−N(1) = 2.143(8)	Mo(1)−N(3) = 2.186(6)
Mo(1)−N(2) = 2.161(7)	Mo(1)−N(2) = 2.156(8)	Mo(1)−N(4) = 2.236(6)
Mo(2)−O(2) = 2.153(6)	Mo(2)−O(4) = 2.116(7)	Mo(2)−N(5) = 2.232(5)
Mo(2)−O(4) = 2.134(5)	Mo(2)−O(1) = 2.134(8)	Mo(2)−N(6) = 2.183(6)
Mo(2)−N(3) = 2.164(6)	Mo(2)−N(4) = 2.140(9)	Mo(2)−N(7) = 2.183(6)
Mo(2)−N(4) = 2.163(7)	Mo(2)−N(5) = 2.161(8)	Mo(2)−N(8) = 2.232(6)
		Li(1)−N(4) = 2.200(15)
O(1)−Mo(1)−N(1) = 90.2(2)	O(2)−Mo(1)−O(3) = 86.7(3)	Li(1)−C(19) = 2.290(15)
O(1)−Mo(1)−O(3) = 88.4(2)	O(2)−Mo(1)−N(1) = 157.1(3)	Li(1)−C(20) = 2.350(15)
N(1)−Mo(1)−O(3) = 160.6(2)	O(3)−Mo(1)−N(1) = 88.9(3)	Li(1)−C(21) = 2.280(17)
O(1)−Mo(1)−Mo(2) = 92.31(16)	O(2)−Mo(1)−Mo(2) = 91.2(2)	Li(1)−C(22) = 2.180(16)
O(3)−Mo(1)−Mo(2) = 90.52(16)	O(3)−Mo(1)−Mo(2) = 91.2(2)	Li(1)−C(27) = 2.233(17)
O(1)−Mo(1)−N(2) = 153.92(2)	N(1)−Mo(1)−Mo(2) = 111.4(2)	Li(1)−C(28) = 2.361(16)
N(1)−Mo(1)−N(2) = 85.6(2)	O(2)−Mo(1)−N(2) = 90.1(3)	Li(1)−C29) = 2.409(15)
O(3)−Mo(1)−N(2) = 87.32(2)	O(3)−Mo(1)−N(2) = 157.6(3)	Li(1)−C(30) = 2.364(15)
Mo(2)−Mo(1)−N(2) = 113.45(16)	N(1)−Mo(1)−N(2) = 85.5(3)	
O(1)−Mo(1)−K(1) = 45.98(16)	Mo(2)−Mo(1)−N(2) = 111.0(2)	N(1)−Mo(1)−N(3) = 137.6(3)
N(1)−Mo(1)−K(1) = 49.77(17)	O(4)−Mo(2)−N(4) = 89.9(3)	N(1)−Mo(1)−N(2) = 83.8(3)
O(3)−Mo(1)−K(1) = 119.30(17)	O(1)−Mo(2)−N(4) = 157.0(3)	N(3)−Mo(1)−N(2) = 90.3(2)
Mo(2)−Mo(1)−K(1) = 122.06(4)	O(4)−Mo(2)−Mo(1) = 90.73(19)	N(1)−Mo(1)−N(4) = 90.9(3)
N(2)−Mo(1)−K(1) = 116.19(17)	O(1)−Mo(2)−Mo(1) = 90.92(2)	N(3)−Mo(1)−N(4) = 83.6(2)
O(4)−Mo(2)−O(2) = 86.5(2)	N(4)−Mo(2)−Mo(1) = 111.8(2)	N(2)−Mo(1)−N(4) = 164.2(2)
O(4)−Mo(2)−Mo(1) = 90.76(16)	O(4)−Mo(2)−N(5) = 157.2(3)	N(1)−Mo(1)−Mo(2) = 111.09(19)
O(2)−Mo(2)−Mo(1) = 89.11(16)	O(1)−Mo(2)−N(5) = 89.7(3)	N(3)−Mo(1)−Mo(2) = 111.35(17)
O(4)−Mo(2)−N(4) = 91.1(2)	N(4)−Mo(2)−N(5) = 85.0(3)	N(2)−Mo(1)−Mo(2) = 98.10(19)
O(2)−Mo(2)−N(4) = 161.0(2)	Mo(1)−Mo(2)−N(5) = 111.8(2)	N(4)−Mo(1)−Mo(2) = 97.67(16)
Mo(1)−Mo(2)−NO(4) = 109.81(17)		N(7)−Mo(2)−N(6) = 140.2(2)
O(4)−Mo(2)−N(3) = 153.9(2)		N(7)−Mo(2)−N(5) = 89.9(2)
O(2)−Mo(2)−N(3) = 89.4(2)		N(6)−Mo(2)−N(8) = 83.8(2)
Mo(1)−Mo(2)−N(3) = 115.00(17)		N(7)−Mo(2)−N(8) = 84.3(2)
N(4)−Mo(2)−N(3) = 84.5(2)		N(6)−Mo(2)−N(8) = 90.4(2)
		N(5)−Mo(2)−N(8) = 163.0(2)
		N(7)−Mo(2)−Mo(1) = 109.28(17)
		N(6)−Mo(2)−Mo(1) = 110.51(16)
		N(5)−Mo(2)−Mo(1) = 98.36(16)
		N(8)−Mo(2)−Mo(1) = 98.61(17)

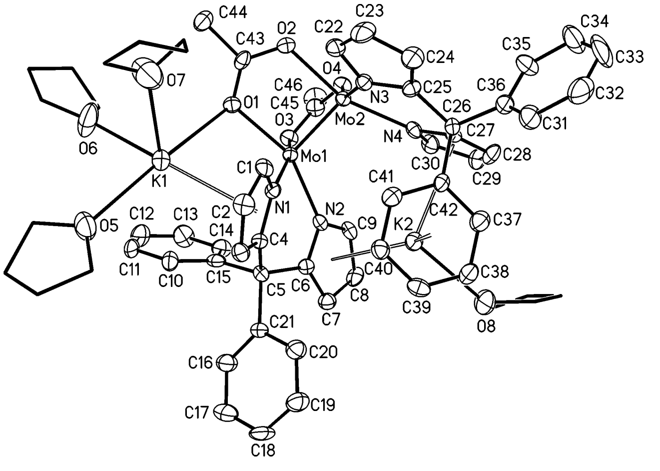


Figure 1. Thermal ellipsoid plot of **1**. Thermal ellipsoids are drawn at 30% probability.

O(3) = 91.2(2)°]. The two distorted planes defined by the donor atoms around each Mo are not parallel but skewed as a result of the coordination of the two potassium atoms which adopt a nearly identical bonding mode with the ligand system. Each potassium is π-bonded to two pyrrolide rings from two different ligands [K(1)−N(1) = 2.976(8) Å, K(1)−C(1) = 3.051(10) Å, K(1)−C(2) = 3.150(11) Å, K(1)−C(3) = 3.12(10) Å, K(1)−C(4) = 3.010(10) Å] and to the two N atoms of the pyridine residues [K(1)−N(6) = 3.005(10) Å] each adopting a curious bridging mode between the two potassium atoms.

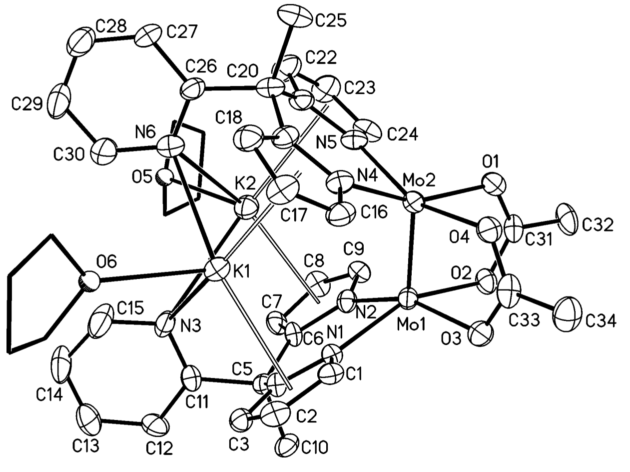


Figure 2. Thermal ellipsoid plot of **2**. Thermal ellipsoids are drawn at 30% probability.

Compound 3. The coordination geometry around each Mo (Figure 3) can be described in terms of distorted trigonal bipyramid [N(2)−Mo(1)−N(4) = 164.2(2)°, N(1)−Mo(1)−N(3) = 137.6(3)°, N(1)−Mo(1)−N(2) = 83.8(3)°, N(3)−Mo(1)−N(4) = 83.6(2)°, N(3)−Mo(1)−N(2) = 111.35(17)°, N(1)−Mo(1)−N(4) = 90.9(3)°] with the second Mo atom occupying one equatorial position [Mo(2)−Mo(1)−N(1) = 111.09(19)°, Mo(2)−Mo(1)−N(2) = 98.10(19)°, Mo(2)−Mo(1)−N(3) = 111.35(17)°, Mo(2)−Mo(1)−N(4) = 97.67(16)°]. The other four coordination sites are occupied by the four rings N donor atoms with each dipyrrolide occupying

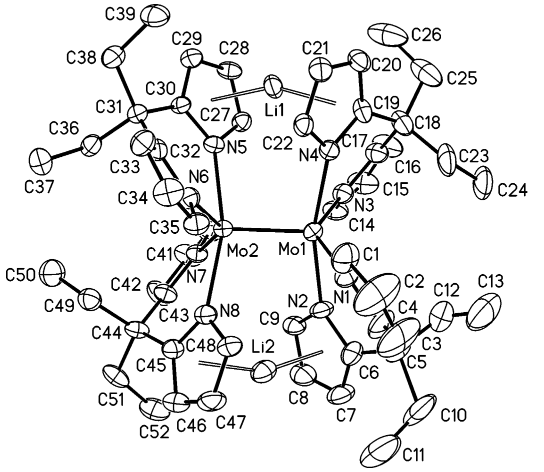


Figure 3. Thermal ellipsoid plot of **3**. Thermal ellipsoids are drawn at 30% probability.

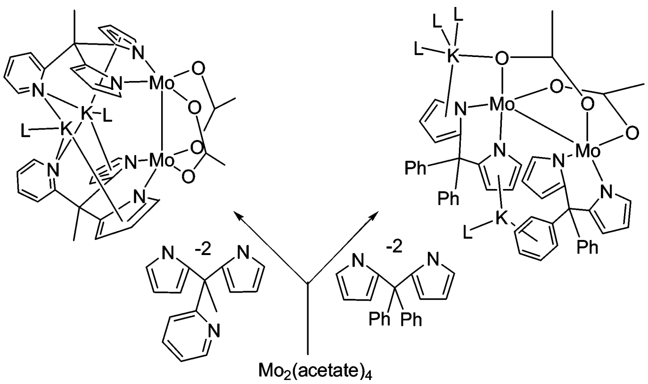
one axial [Mo(1)−N(4) = 2.236(6) Å, Mo(1)−N(2) = 2.232(6) Å] and one equatorial position [Mo(1)−N(1) = 2.175(7) Å, Mo(1)−N(3) = 2.186(6) Å]. The connection between the two units is realized via a short Mo−Mo bonding contact and through two lithium atoms each π-bonded to two pyrrolyl rings [Li(1)−N(4) = 2.200(15) Å, Li(1)−C(19) = 2.290(15) Å, Li(1)−C(20) = 2.350(15) Å, Li(1)−C(21) = 2.280(17) Å, Li(1)−C(22) = 2.180(16) Å] of two ligands from two different units and in an overall bent-metallocene type of arrangement. Interestingly, the two units forming the dimer are not eclipsed but nearly perfectly staggered (torsion angle N−Mo(1)−Mo(2)−N ranging between 49.8 and 42.4°, average torsion angle 45.0°). Two additional alkali metal cations are present in the lattice and are each solvated by four molecules of THF and unconnected to the dianionic moiety.

DFT Calculations. Theoretical calculations were performed on a cluster of computers by using the LINUX operating systems and the ADF software package (version ADF2000.02).[14a−c] The calculations were performed at the nonlocal DFT level of theory using the exchange functional of Becke[14d] and the correlation functional of Perdew.[14e] Uncontracted Slater-type orbitals (STOs) were user as a basis functions for the SCF calculations.[14f] Double-ξ basis set have been used for all elements. The $(1s)^2$ core electrons of carbon, nitrogen, oxygen, (1s2s2p3s3p3d)[28] of molybdenum were treated by the frozen-core approximation.[14g] A standard Mulliken population analysis was carried out to obtain total atomic populations and charges; atomic contributions were also determined for selected individual molecular orbitals.

Results and Discussion

For the preparation of divalent Mo dipyrrolide complexes we have avoided synthetic routes requiring reduction of higher valent precursors since problems may arise from the possible reactivity of highly reactive midvalent intermediates with dinitrogen, solvents, or even unreacted starting materials. Thus, we have attempted the reactions of $Mo_2Cl_8K_4$ and $Mo_2(acetate)_4$, both containing the metal in the final divalent state, with the dipotassium salt of the dipyrrolide dianion $[Ph_2C(2\text{-}C_4H_3N)_2]K_2$. While the $Mo_2Cl_8^{4-}$ complex proved to be totally unreactive under a variety of reaction conditions, ligand replacement was obtained under mild conditions in the case of $Mo_2(acetate)_4$. As anticipated, the nucleophilic strength of the dipyrrolide dianion was not sufficient to completely replace the four acetate groups of $Mo_2(acetate)_4$ (Scheme 1). The reaction afforded the diamagnetic and dinuclear $\{[Ph_2C(2\text{-}C_4H_3N)_2]_2Mo_2(OAc)_2[K(THF)_3][K(THF)]\}\cdot THF$ (**1**). The formulation obtained by the X-ray crystal structure (Figure 1) was in agreement with both analytical and NMR data, clearly showing the presence of both the acetate groups and the characteristic resonances of the dipyrrolide ligand in the appropriate intensity ratio. The Mo−Mo distance [Mo(1)−Mo(2) = 2.1561(9) Å] falls in the normal range of diamagnetic cofacial or lantern-type divalent dimers. The *cis*-$Mo_2(OAc)_2$ motif is very similar to that of other *cis*-$Mo_2(OAc)_2(amidinate)_2$ compounds known in the literature.[16]

Scheme 1



A further attempt to obtain a carboxylate-free dinuclear complex of a dipyrrolyl anion was made by introducing an additional pyridine moiety in the dipyrrolide ligand framework by preparing the new 2-[1,1-bis(1*H*-pyrrol-2-yl)ethyl]pyridine ligand. The starting point for the tailoring of this particular ligand was the observation that quadruply bonded systems may show sensitivity to axial ligation.[2] Although Mo is much less sensitive[17] than Cr due to the substantial strength of the Mo−Mo quadruple bonds, it has nevertheless been observed that the axial coordination of pyridine is indeed capable of elongating the Mo−Mo distance.[18] Therefore, the presence of an additional pyridine ring in the dipyrrolide framework, placed at a bonding distance but with a geometry constraint that will prevent the formation of an axially ligated lantern-type of structure, might result in a substantially different ligand field. This was expected to ultimately affect the Mo−Mo bond multiplicity. In addition, molecular modeling and geometry optimization have shown that this new ligand could provide a desirable tripodal-like type of arrangement which could weaken the quadruple Mo−Mo bond by distorting the normal square-planar or square-pyramidal coordination geometry around the Mo atom.

The ligand was easily prepared via condensation of pyrrole with acetylpyridine. The deprotonation of the resulting 2-[1,1-bis(1*H*-pyrrol-2-yl)ethyl]pyridine was carried out with KH in THF and the dipotassium salt generated in situ was reacted with $(AcO)_4Mo_2$. The reaction afforded the diamagnetic and dinuclear {[2-[1,1-bis(1*H*-pyrrol-2-yl)ethyl]pyridine]Mo-

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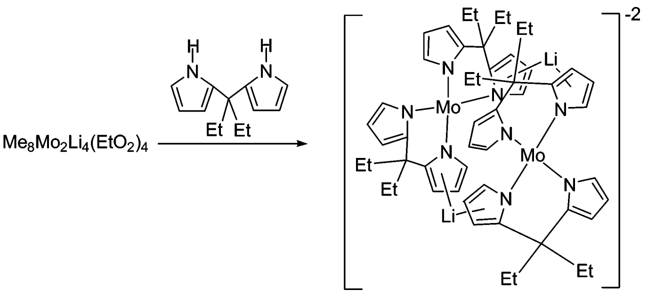
(16) Zou, G.; Ren, T. *Inorg. Chim. Acta* **2000**, *304*, 305.

(17) Cotton, F. A.; Extine, M.; Gage, L. D. *Inorg. Chem.* **1978**, *17*, 172.

(18) Cotton, F. A.; Norman, J. G., Jr. *J. Am. Chem. Soc.* **1972**, *94*, 5697.

Scheme 2



$(OAc)[K(THF)]\}_2\cdot THF$ (**2**) where, to our disappointment, two acetate groups were still retained by the Mo_2 unit (Figure 2). Basically, the ligand adopted the tripodal bonding mode with K rather than with Mo and, in doing so, engaged in a considerable amount of π-interactions with K. Conversely, the ligand acted as a simple bidentate σ-ligand for the divalent Mo atoms, clearly emphasizing the substantial stabilization provided by the two bridging acetate residues toward the Mo_2 unit. In view of the value of the Mo−Mo distance [Mo(1)−Mo(2) = 2.1475(14) Å], the diamagnetism of the complex was just as expected.

Since attempts to prepare an acetate-free complex were unsuccessful while using $Mo_2(acetate)_4$ as a starting material, we have tested the possibility of using $(CH_3)_8Mo_2\,Li_4(Et_2O)_4$ instead, allowing ligand replacement with the dipyrrole via simple proton exchange and elimination of methane. However, it was anticipated that lithium atoms would most likely be retained, thus affording electron-rich -ate types of structures.[19]

The reaction of diethyldipyrrolylmethane $Et_2C(C_4H_3NH)_2$ with $(CH_3)_8Mo_2Li_4(Et_2O)_4$ (Scheme 2) occurred instantly at room temperature affording the dinuclear $\{[Et_2C(C_4H_3N)_2]_4$-$Mo_2Li_2\}\{Li(THF)_4\}_2\cdot 0.5THF$ (**3**), which was isolated in crystalline form and acceptable yield. The molecular connectivity was yielded by an X-ray crystal structure (Figure 3) showing a dimolybdenum unit in which each of the two Mo atoms is surrounded by two dipyrrolide ligands and staggered by 45° with respect to the other. Each ligand acts as a regular chelating ligand, σ-bonding the metals with the pyrrolyl rings N donor atoms. We found no evidence that the two bridging lithium atoms could be removed by coordination of TMEDA.

The Mo−Mo distance of **3** is rather short [Mo(1)−Mo(2) = 2.2464(9) Å] and in agreement with the presence of a Mo−Mo multiple bond. However, the distance falls in the upper limit for a quadruply bonded system of a cofacially metal−metal-bonded dimolybdenum unit.[20] The complex is paramagnetic (Figure 4) with a magnetic moment rising sharply in the range 0−15 K, from an intercept value of about 0.8 μ_B/mol to a value of about 1.2 μ_B. After that, the increase is nearly steadily to a room-temperature value of 3.5 μ_B. Unfortunately, the data could not be fit with a simple antiferromagnetically coupled model.

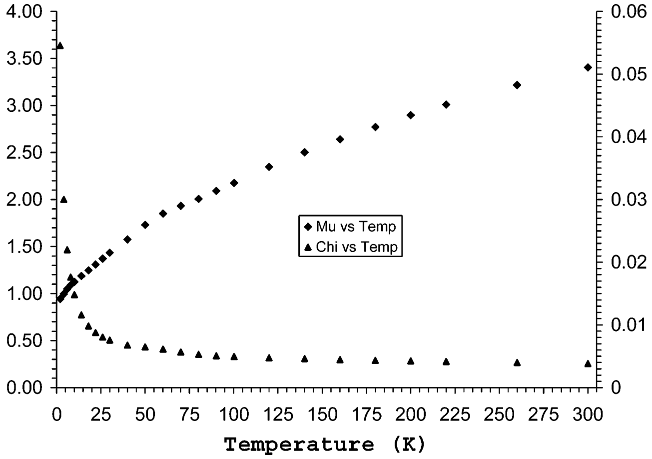


Figure 4. Plot of the magnetic susceptibility and of the magnetic moment versus *T* for **3**.

The magnetism of **3** is rather surprising for a divalent Mo_2 unit with such a short intermetallic distance and is most likely to be ascribed to the 45° staggering angle between the two Mo moieties. The value of the intermetallic distance per se does not justify the presence of magnetism since complexes with Mo−Mo distances up to 2.3 Å are known and are invariably diamagnetic.[21] For example, the porphyrinato dimer,[22] which is the closest to **3** in terms of similarity of ligand system and which displays a comparable Mo−Mo distance (2.239 Å) with a substantial staggering angle of 36°, is diamagnetic. To the best of our knowledge, the only exception is provided by β-$Mo_2Cl_4(L-L)_2$ (L−L = bidentate phosphine) in which there are twist angles covering the range from 0 to 40°. In the case of the complex with a twist angle of 40° [L−L = 1,2-bis(dimethylphosphino)ethane] the dependence of the magnetic properties on *T* clearly indicates the presence of a weak antiferromagnetic exchange.[23,24] However, this does not seem to be the case for **3**, whose magnetic behavior is more complex and possibly the result of a combination of phenomena. The extent of the magnetism also provides, in combination with the Mo−Mo distance, a convincing argument against other possibilities such as that complex **3** could actually be either a class III mixed-valence[25] Mo(II)/Mo(III) monohydride or a trivalent dihydride. Thus, the divalent state seems to be the most realistic scenario for **3**. Accordingly, the UV−vis spectrum of **3** shows three shoulders at 463, 594, and 739 nm (Figure 5). The last one is rather weak and in the region one could expect for a $^1(\delta^2)-{}^1(\delta\delta^*)$ transition.

Density functional theory calculations have predicted both the strength of the covalent bonding in the divalent Mo_2 unit

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(19) Ganesan, M.; Bérubé, C. D.; Gambarotta, S.; Yap, G. P. A. *Organometallics* **2002**, *21*, 1707.

(20) Cotton, F. A.; Daniels, L. M.; Hillard, E. A.; Murillo, C. A. *Inorg. Chem.* **2002**, *41*, 2466.

(21) (a) Kutchta, M. C.; Cloke, F. G. N.; Hitchcock, P. B. *Organometallics* **1998**, *17*, 1934. (b) Cotton, F. A.; Koch, S. A.; Schultz, A. J.; Williams, J. M. *Inorg. Chem.* **1978**, *17*, 2093.

(22) Yang, C. H.; Dzugan, S. J.; Goedken, V. L. *J. Chem Soc., Chem. Commun.* **1986**, 1313.

(23) Hopkins, M. D.; Zietlow, T. C.; Miskowski, V. M.; Gray, H. B. *J. Am. Chem. Soc.* **1985**, *107*, 510.

(24) Cotton, F. A.; Eglin, J. L.; Hong, B.; James, C. A. *J. Am. Chem. Soc.* **1992**, *114*, 4915.

(25) Robin, M. B.; Day, P. *Adv. Inorg. Chem. Radiochem.* **1967**, *10*, 247.

(26) A crystallographic database search yielded 71 hits of diamagnetic Mo(III) compounds in the range of Mo−Mo distances 2.00−2.25 Å.

Table 3. Percent Mulliken Contribution of Various Atomic Orbitals in the Relevant MOs of **3**

	spin A		spin B	
orbital, energy (eV)	Mo(1)%, AO	Mo(2)%, AO	Mo(1)%, AO	Mo(2)%, AO
HOMO-11, −3.90	11.88, d(z^2) 4.34, d(yz) 2.04, d(xz)	9.78, d(z^2) 1.76, d(yz)	9.71, d(z^2) 3.29, d(yz) 1.61, d(xz)	12.89, d(z^2) 2.36, d(yz) 1.05, d(xz)
HOMO-6, −3.30	18.92, d(z^2) 3.28, d(xz) 1.74, s 1.12, d(xy)	11.56, d(z^2) 2.93, d(xz)	17.15, d(z^2) 1.30, s	18.43, d(z^2) 1.59, d(xz) 1.46, d(yz)
HOMO-5, −3.21	9.26, d(z^2)	7.51, d(z^2) 1.27, d(yz)	4.50, d(z^2) 2.33, d(xz) 1.50, d(yz)	6.76, d(z^2) 4.59, d(yz) 1.43, d(xz)
HOMO-4, −3.18	31.96, d(xz) 6.59, d(xy)	14.74, d(xz) 9.72, d(xy)	18.87, d(xz) 5.60, d(yz)	18.85, d(xz) 15.25, d(yz)
HOMO-3, −2.99	1.17, d(z^2)	1.16, d(z^2)	0	1.25, d(z^2)
HOMO-2, −2.71	2.30, d(yz)	2.50, d(yz)	1.44, d(yz)	2.76, d(yz)
HOMO-1, −2.61	17.25, d(yz) 7.88, d(xz) 2.62, p(y) 1.19, d(xy)	18.17, d(yz) 2.40, d(xz) 1.06, p(y)	10.67, d(xz) 9.50, d(yz)	17.59, d(yz) 7.03, d(xz) 1.85, p(y) 1.05, p(x)
HOMO, −2.27	61.04, d(xy) 8.96, d($x^2 - y^2$)	0	0	15.03, d(xy) 60.98, d($x^2 - y^2$)
LUMO, −2.25	8.70, d(xy) 1.28, d($x^2 - y^2$)	0	0	3.54, d($x^2 - y^2$)
LUMO+1, −2.14	0 from all Mo 28.23 (Li) tot. percentage for different AOs		1.02, d($x^2 - y^2$) from Mo(2) 27.69 (Li) tot. percentage for different AOs	

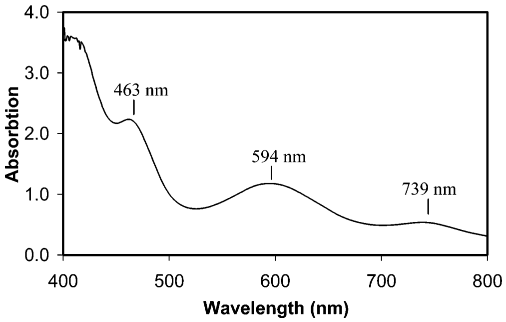

Figure 5. Optical spectrum of **3**.

and also that diamagnetism should be expected for Mo−Mo distance up to 2.5 Å.[3b] However, a 45.0° staggering of the two Mo-containing units is expected to degenerate the δ and δ^* orbitals of a quadruply bonded Mo_2 unit. Despite this, the $\delta-\delta^*$ transition energy is expected to be nonzero for a molecule in either a singlet or a triplet state as a result of differences in electron repulsion and correlation energy between the two states.[2c,24] This might well explain both the magnetic and spectroscopic behaviors of complex **3**, clearly showing the presence of residual paramagnetism, even at zero K. On the other hand, the presence of the two lithium atoms in the intermetallic region and the consequent twisting of the ligand system may also be a factor that contributes to the partial removal of the degeneracy.

In an attempt to clarify the electronic configuration of **3**, ADF-DFT calculations were performed on the dianion $\{[H_2C(C_4H_3N)_2]_4Mo_2Li_2\}^{2-}$ as a model compound. Given the unique arrangement of the ligand system and the robustness of the coordination of the two bridging lithium atoms, any symmetry constraint seemed unrealistic. The result of the calculation (Table 3) showed that about 80% of the Mo−Mo σ-bonding interaction is realized via three molecular orbitals mainly HOMO-11 (20%), HOMO-6 (40%), and HOMO-5 (20%) respectively located at −3.91, −3.30, and −3.21 eV and all involving a remote part of the ligand system to a different extent. In all three cases, the Mo−Mo interaction is provided by the overlap of the d_{z^2} orbitals. As expected, the two Mo−Mo π-orbitals are identical in shape except for their orthogonal orientation. The first π-orbital (HOMO-4, −3.18 eV) has the two lobes besides the two lithium atoms while the second (HOMO-1, −2.61 eV) has the two lobes oriented against. The different orientation with respect to the two Li atoms appears to be the only reason for the substantial difference in energy betwen these two nearly completely Mo-centered bonds. Obviously, the staggering of the two units implies that the π-bonds are not generated by simple overlaps of d_{xz} or d_{yz} but by hydrid combinations instead. As expected, the HOMO (−2.24 eV) and LUMO (−2.23 eV) are nearly identical in shape with a very small energy gap that nicely accounts for the residual paramagnetism. The two MO's are basically formed by hybrid combinations of $d_{x^2-y^2}$ and d_{xy} with an overall δ nonbonding character. The LUMO+1 (−1.88 eV) is substantially higher in energy and yet sufficiently close to account for the further increment of magnetic moment due to its possible partial population when the T reaches ambient values. The fact that no frontier orbitals engaging the lithium atoms were found seems to rule out the presence of superexchange.

In conclusion, the use of dipyrrolide anions has allowed the preparation and characterization of a unique dimolybdenum complex with a staggering angle of 45°. The resulting paramagnetism of this species is in line with the expectations on the basis of previous theoretical and spectroscopical work.[2c,24] It does not seem, however, to be solely related to antiferromagnetism although theoretical calculations seem to rule out a superexchange-based mechanism. The retention of the two lithium cations in the structure is the factor that leads to the staggering and ultimately to the appearance of paramagnetism. Therefore, it will be interesting to prepare similar dimers with different alkali metal cations that cannot possibly be accommodated in the intermetallic region crowded by the pyrrolide rings. Further work along this line is in progress at the moment.

Acknowledgment. This work was supported by the Natural Sciences and Engineering Council of Canada (NSERC). Prof. L. K. Thompson (Memorial University) is gratefully acknowledged for helping with magnetic measurements and their interpretation.

Supporting Information Available: Listings of atomic coordinates, thermal parameters, and bond distances and angles for structures **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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