Dimolybdenum Bis((*S*,*S*,*S*)-triisopropanolaminate(3−)): A Blue Compound with an Unusual Mo−Mo Triple Bond‡

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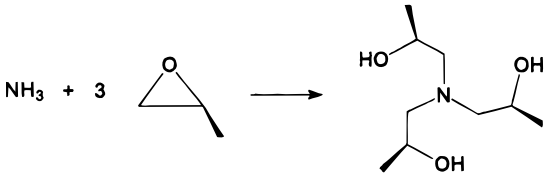
$Mo_2(O^tBu)_6$ and $Mo_2(NMe_2)_6$ each react with (*S*,*S*,*S*)-triisopropanolamine (2 equiv) in benzene to yield dimolybdenum bis((*S*,*S*,*S*)-isopropanolaminate(3−)), $Mo_2[(OC\text{-}(S)\text{-}HMeCH_2)_3N]_2$ (M≡M), as a blue crystalline solid. Cell parameters at −160 °C: $a = 17.389(6)$ Å, $b = 10.843(3)$ Å, $c = 10.463(3)$ Å, $\beta = 125.28(1)°$, $Z = 2$ in space group C2. The molecular structure involves an Mo_2 unit inside an O_6N_2 distorted cubic box. The Mo_2 axis is disordered about three positions with occupancy factors of ca. 45%, 45%, and 10%. Despite this disorder, the molecular structure is shown to contain a central Mo≡Mo unit of distance 2.15(3) Å coordinated to two triolate ligands which each have two chelating arms and one that spans the Mo≡Mo bond. The local $Mo_2O_6N_2$ moiety has approximate C_{2h} symmetry, and the Mo−N distances are long, 2.4 Å. The ^1H and $^{13}C\{^1H\}$ NMR spectra recorded in benzene-d_6 are consistent with the geometry found in the solid-state structure. The blue color arises from weak absorptions, $\epsilon \sim 150$ dm^3 mol^{-1} cm^{-1}, at 580 and 450 nm in the visible region of the electronic absorption spectrum. Raman spectra recorded in KCl reveal pronounced resonance effects with excitation wavelengths of 488.0, 514.5, and 568.2 nm, particularly for the 322 cm^{-1} band, which can probably be assigned to ν(Mo≡Mo). The electronic structure of this compound is investigated by B3LYP DFT calculations, and a comparison is made with the more typical ethane-like (D_{3d}) $Mo_2(OR)_6$ compounds is presented. The distortion imposed on the molecule by the triisopropanolaminate(3−) ligands removes the degeneracy of the M−M π molecular orbitals. The HOMO and SHOMO are both M−M π and M−O σ* in character, while the LUMO is M−M π* and the SLUMO is predominantly M−O σ* with metal sp character. The calculated singlet−singlet transition energies are compared with those implicit in the observed electronic spectrum.

Introduction

The development of the chemistry of triple-bonded complexes of molybdenum and tungsten has principally involved the use of sterically demanding monodentate ligands such as alkyl, alkoxide, amide, thiolate, etc., as in the homoleptic series M_2X_6 or in the mixed-ligated species $M_2X_{6-n}Y_n$, in which $n = 1-3$ and one of the groups X and Y is less sterically demanding than the other, as in the $M_2Cl_2(NMe_2)_4$ compounds.[2,3] Certain bidentate ligands such as carboxylates, carbamates, and dithiophosphates have also been employed, and the central M≡M moiety is preserved in compounds such as $W_2Me_2(O_2CNEt_2)_4$ and $W_2(O_2CNMe_2)_6$.[2,3] Recently, we have been investigating the chemistry of the M_2^{6+} unit with sterically encumbered diolates and biphenoxides.[4−6] The use of these ligands has allowed us to interrogate the mechanisms of substitution about the M_2^{6+} center because the kinetic and thermodynamic products do not interconvert readily. Similarly, with the use of the *p-tert*-butylcalix(4)arene derivatives, we have seen interesting substitution patterns and accessed both dumbbell and bridging (μ-η^2,η^2) forms of coordination.[7] We were attracted to the use of chiral trialkanolamines, such as (*S*,*S*,*S*)-triisopropanolamine, which is readily accessible from the reaction shown in eq 1.



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Nugent and Harlow reported the use of these chiral trialkanolamines in the synthesis of early transition metal alkoxides of the type LTi(O^iPr), LV=O, and $LM(OEt)_2$ (M = Nb, Ta) where L = the trialkanolaminate(3−).[8] We describe here the synthesis of the Mo_2L_2 compound, where L = (*S*,*S*,*S*)-triisopropanolaminate(3−), which, as a result of the steric constraints of the ligand and the propensity of the metal atoms to maintain an unbridged Mo≡Mo bond, has an unusual structure wherein the degeneracy of the typical cylindrical triple bonds seen for M_2X_6 compounds is removed.

‡ This paper is dedicated to Professor F. A. Cotton on the occasion of his 70th birthday.

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Results and Discussion

Synthesis. The reactions of $Mo_2(O^tBu)_6$[9] and $Mo_2(NMe_2)_6$[10] with (*S*,*S*,*S*)-triisopropanolamine, LH_3 (2 equiv), in benzene lead to the formation of Mo_2L_2 in essentially quantitative yield. Crystallization from benzene yields blue crystals of Mo_2L_2 which are air stable for short periods of time (∼1 day). Related reactions involving $W_2(O^tBu)_6$[11] and $W_2(NMe_2)_6$[12] yield a green compound which is thermally unstable and has not been properly characterized beyond obtaining an ^1H NMR spectrum from a freshly prepared sample. By analogy with the ^1H NMR spectrum of Mo_2L_2 (vide infra), we can postulate that the structure of W_2L_2 is analogous to that of Mo_2L_2. Why the ditungsten complex is thermally unstable is not clear.

Reactions of $M_2(O^tBu)_6$ and $M_2(NMe_2)_6$, where M = Mo or W, with triethanolamine in benzene yield brown precipitates which are insoluble in hydrocarbon solvents and other common organic solvents. We believe that these products are oligomers and propose that the presence of the methyl group (or possibly other alkyl groups) is necessary for steric protection of the central M_2^{6+} unit.

NMR Spectra. The ^1H NMR spectra of Mo_2L_2 in toluene-d_8 are essentially temperature independent. There are three methyl doublets at high field, ca. 1.2 ppm, and three methine resonances, two at low field, 5.5 and 5.3 ppm, and one at notably higher field, 3.4 ppm. Clearly, there are three different orientations of the $OCHMeCH_2$ groups with respect to the Mo≡Mo bond and the magnetic anisotropy of the latter is responsible for the shielding and deshielding effects on the methine protons. A COSY spectrum was obtained which allowed the connectivity of the resonances to be established for each $OCHMeCH_2$ group. Data are given in the Experimental Section.

Solid-State Crystal and Molecular Structures. The blue crystals of Mo_2L_2 proved to be troublesome with respect to obtaining a satisfactory molecular structure by single-crystal X-ray crystallography. Crystals were obtained from a variety of solvents (benzene, toluene, and THF), but in all cases, the solutions of the structures had a common problem. The structural work reported here was performed on a crystal grown in benzene which had the solvate formula $Mo_2L_2 \cdot 2C_6H_6$.

In the space group *C*2, there are two equivalent molecules in the unit cell. The problem with the solution is a common one for molecules of the type wherein an M_2^{n+} unit is inside a box, namely, that while the ligand atom positions are relatively well defined (fixed), the Mo−Mo axis is disordered over three possible positions.[13] In this case, the O_6N_2 skeleton conforms to a distorted cube and the Mo_2^{6+} unit is disordered principally about two positions with equal occupancy, 45%, and to a lesser extent, 10%, about the third.

A ball-and-stick drawing of the molecular structure is shown in Figure 1. Each molecule has a crystallographically imposed C_2 axis of symmetry, and the central $Mo_2N_2O_6$ core has virtual C_{2h} symmetry. Listings of selected bond distances and bond angles for the three disordered molecules are given in Tables 1 and 2. With the disorder, the agreement of M−M, M−O, and M−N distances is poor. However, there is no doubt about the basic coordination geometry of the Mo_2^{6+} unit being that shown in Figure 1. (The minor disordered molecule has the crystallographic C_2 axis perpendicular to the M−M axis.) Of particular note is the fact that the Mo−N distances are very long, ca. 2.4 Å, indicative of very weak N to Mo bonding. The M−M distances are typical for an $(Mo{\equiv}Mo)^{6+}$ unit.[2] The local MoO_3 coordination is that of a distorted T, and thus the Mo_2O_6 skeleton may be related to that of the typical D_{3d}-$Mo_2(OR)_6$ geometry, as shown in Figure 2.

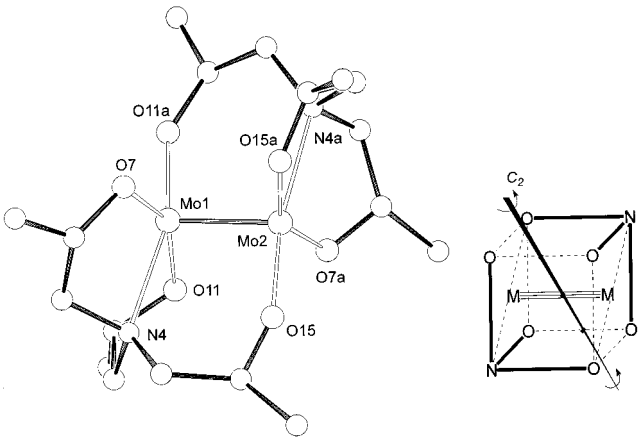

Figure 1. Ball-and-stick drawing of Mo_2L_2 showing one of the principal orientations of the Mo−Mo unit.

Table 1. Selected Bond Distances (Å) of Mo_2L_2

Mo(1)−Mo(2)	2.1770(11)	Mo(2)−O(15a)	1.944(7)
Mo(1)−O(7)	1.897(5)	Mo(2)−N(4a)	2.356(5)
Mo(1)−O(11)	1.859(9)	Mo(3)−Mo(3)	2.14(2)
Mo(1)−O(11a)	2.017(9)	Mo(3)−O(7)	2.06(1)
Mo(1)−N(4)	2.382(5)	Mo(3)−O(11)	1.76(2)
Mo(2)−O(7)	2.018(6)	Mo(3)−O(15)	2.07(2)
Mo(2)−O(15)	1.884(7)	Mo(3)−N(4)	2.44(1)

Table 2. Selected Bond Angles (deg) of Mo_2L_2

Mo(2)−Mo(1)−O(7)	101.3(3)	O(7a)−Mo(2)−O(15)	98.6(3)
Mo(2)−Mo(1)−O(11)	103.7(3)	O(7a)−Mo(2)−N(4a)	72.1(2)
Mo(2)−Mo(1)−O(11a)	94.3(3)	O(15a)−Mo(2)−O(15)	98.7(7)
Mo(2)−Mo(1)−N(4)	97.8(3)	O(15a)−Mo(2)−N(4)	83.8(4)
O(7)−Mo(1)−O(11)	146.7(3)	O(15)−Mo(2)−N(4)	158.7(3)
O(7)−Mo(1)−O(11a)	99.5(3)	Mo(3a)−Mo(3)−O(7a)	94.1(6)
O(7)−Mo(1)−N(4)	73.4(2)	Mo(3a)−Mo(3)−O(11)	102.3(6)
O(11)−Mo(1)−O(11a)	100.1(7)	Mo(3a)−Mo(3)−O(15)	100.2(4)
O(11)−Mo(1)−N(4)	81.7(4)	Mo(3a)−Mo(3)−N(4)	96.4(6)
O(11a)−Mo(1)−N(4)	167.0(3)	O(7a)−Mo(3)−O(11)	102.7(9)
Mo(1)−Mo(2)−O(7a)	97.3(2)	O(7a)−Mo(3)−O(15)	93.3(8)
Mo(1)−Mo(2)−O(15)	99.1(3)	O(7a)−Mo(3)−N(4)	167.3(8)
Mo(1)−Mo(2)−O(15a)	102.1(3)	O(11)−Mo(3)−O(15)	151.2(6)
Mo(1)−Mo(2)−N(4a)	101.1(2)	O(11)−Mo(3)−N(4)	81.9(7)
O(7a)−Mo(2)−O(15a)	151.5(2)	O(15)−Mo(3)−N(4)	77.9(6)

Electronic Spectra. The electronic absorption spectra recorded in hexane and THF in the visible region are shown in Figure 3, and the CD spectrum recorded in THF is shown in Figure 4. The blue color clearly arises from the absorptions at $\lambda_{max} \sim 580$ and 450 nm, which have $\epsilon \sim 150$ and 100 $dm^3\ mol^{-1}\ cm^{-1}$, respectively. At shorter wavelengths, there is also a shoulder at $\lambda \sim 380$ nm, and at ca. 300 nm, intense charge-transfer bands (O to M) are observed.

The observation of a band at 580 nm is most unusual for d^3-d^3 triply bonded complexes and certainly warrants attention. Complexes having the formula M_2X_6 with ethane-like geometries are pale yellow or orange as the result of a tailing into the visible region of the spectrum of a band at ca. 300 nm arising from the M−M π to M−M $(\pi/\delta)^*$ transition.[14] To interrogate

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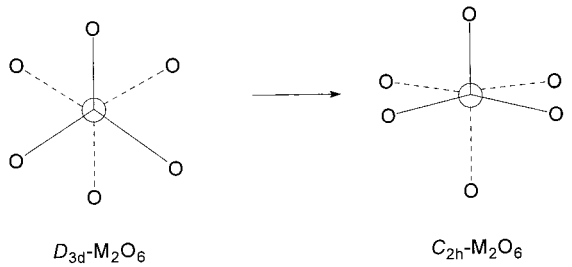

Figure 2. The D_{3d}-$Mo_2(OH)_6$ to C_{2h}-$Mo_2(OH)_6$ distortion shown as a Newman projection.

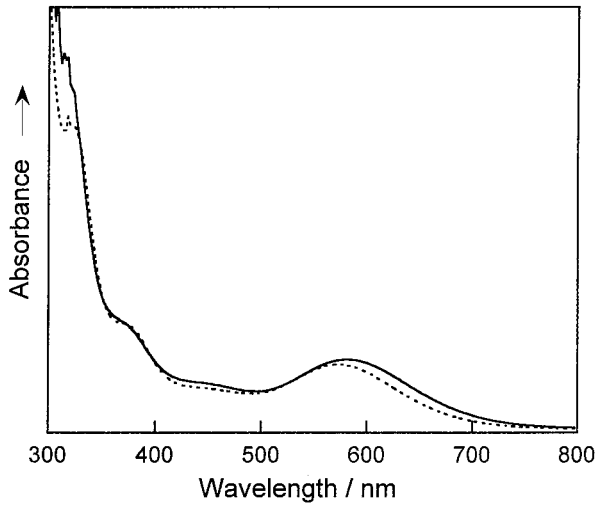

Figure 3. Visible absorption spectra of Mo_2L_2 in hexane (solid line) and THF (dotted line).

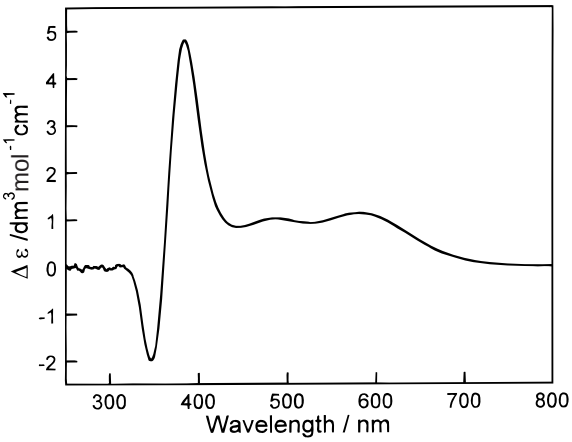

Figure 4. CD spectrum of Mo_2L_2 in THF.

the electronic structure of Mo_2L_2, we undertook various molecular orbital calculations.

Computed Structure. By using the B3LYP DFT computational method, with the LANL2MB effective core potential and basis set, we examined the electronic structure of an idealized D_{3d}-$Mo_2(OH)_6$ molecule with Mo−Mo = 2.19 Å, Mo−O = 1.89 Å, and Mo−Mo−O = 103°, which are typical structural features for a $Mo_2(OR)_6$ compound. The HOMO is a degenerate orbital of e_u symmetry having principally M−M d_π−d_π character. The LUMO is the M−M δ* orbital, e_g, which has some M−O π* character. The SLUMO is of a_u symmetry and is principally M−M (d_{z^2}−d_{z^2}) σ* in character, while the next highest orbital is the vacant degenerate M−M (p−p) π bonding

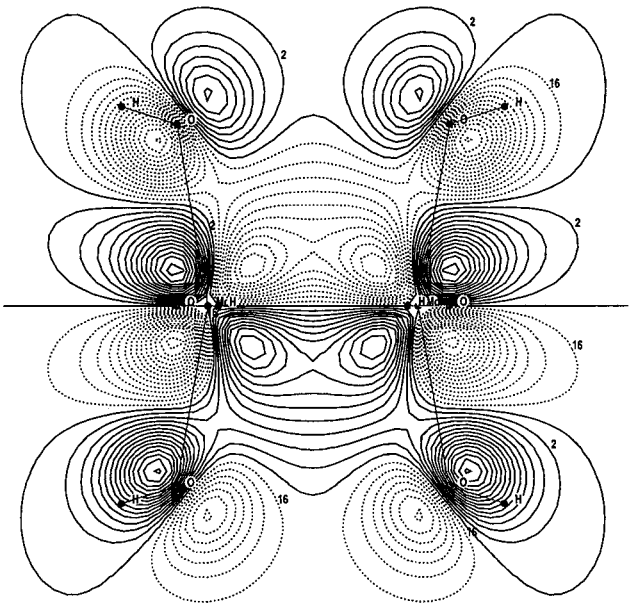

Figure 5. Contour plot of the HOMO drawn perpendicular to the σ_h plane.

orbital of e_u symmetry. These findings parallel other investigations of the electronic structure of $Mo_2(OR)_6$ molecules.[2]

To approximate the observed structure, calculations were performed on a molecule of the formula $Mo_2(OH)_6(NH_3)_2$ where the $Mo_2O_6N_2$ skeleton was taken from the observed structure and the O−H bonds were substituted for O−C bonds. This low-symmetry molecule was subsequently sacrificed in favor of an idealized $Mo_2(OH)_6$ structure with C_{2h} symmetry. The removal of the NH_3 ligands and the transformation to the idealized C_{2h} symmetry did not significantly change the orbital energies of the frontier MO's but did allow us to attempt to classify the MO's into σ, π, and δ components.

For a C_{2h}-$Mo_2(OH)_6$ molecule, the M−M π orbitals are not degenerate and care must be taken to plot these orbitals in the appropriate plane. The HOMO is of a_u symmetry and the SHOMO of b_u symmetry. Both are M−M d_π−d_π bonding and M−O antibonding. They are shown in Figures 5 and 6, respectively, where it can be seen that the HOMO has a greater percentage of M−O π* antibonding character. The calculated difference in energy between these orbitals is ca. 0.6 eV.

The LUMO is shown in Figure 7. It has a_g symmetry and is primarily M−M π* in character. The SLUMO is of b_u symmetry and has primarily M−O σ* character with metal s−p mixing. This is shown in Figure 8. The next highest orbital is shown in Figure 9 and has primarily oxygen lone pair character with some M−M (p_π−p_π) π* contribution. In all of these orbitals, it is important to recognize how a classification such as M−M σ, π, or δ is compromised by the metal−oxygen admixture and by the lower symmetry of the complex.

These simple calculations show that the M−M frontier orbitals of the C_{2h}-$Mo_2(OH)_6$ molecule are very different from those of the D_{3d}-(ethane-like)$Mo_2(OH)_6$ molecule, where the orbitals all transform as "a" or "e".

The orbital energies deduced from the calculations are listed in Table 3 for the C_{2h}-$Mo_2(OH)_6$ molecule. The HOMO−LUMO singlet transition is predicted to be the symmetry-allowed a_u to a_g orbital (a filled π to π* type transition), and it is not unreasonable to assign this to the observed absorption at λ_{max} ~580 nm, which causes this compound to be blue. The a_u(HOMO) to b_u(SLUMO) transition, which in C_{2h} symmetry is orbitally forbidden, may well correspond to the weaker band

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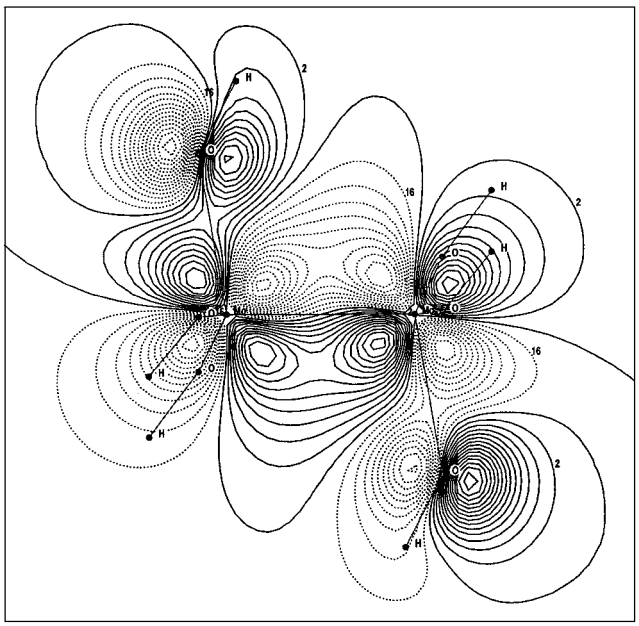

Figure 6. Contour plot of the SHOMO drawn in the σ_h plane.

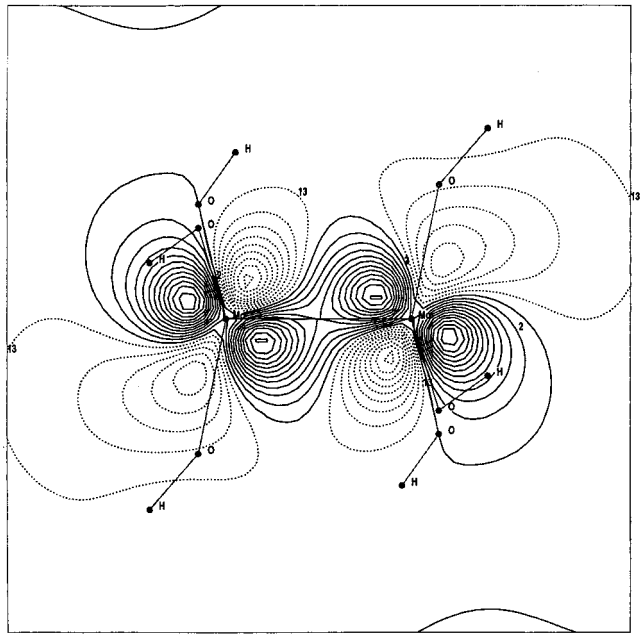

Figure 7. Contour plot of the LUMO drawn in the σ_h plane.

at λ_{max} ~450 nm; the $a_u \rightarrow b_g$ (M−M $p_\pi - p_\pi$, π^*) transition is allowed and would be expected to have a much higher intensity, possessing significant metal d → p character.

Raman Spectra. The assignment of ν(M−M) in the spectra of D_{3d}-M_2X_6 compounds, where X = NMe_2 or OR (M = Mo or W), has proved problematic because of extensive coupling with metal−ligand vibrations.[10,12] However, for certain $M_2(OR)_6$ compounds, the assignment of ν(M≡M) has been proposed.[15] For the now classical quadruply bonded $M_2X_8^{n-}$ complexes with D_{4h} symmetry, the assignment of ν(M−M) shows a similar complication as a function of X and the M−M−X angle.[16−18] In the present case, the $Mo_2O_6N_2$ unit has approximately C_{2h} symmetry, so the Mo−O stretches span $2A_g + B_g + A_u + 2B_u$, the MoN stretches span $A_g + B_u$, and the Mo−Mo stretch is designated as A_g. Five bands are therefore expected in the low-wavenumber region of the Raman spectrum. The Mo≡Mo triple-bond stretch is typically found near 360 cm^{-1}.[2] For $Mo_2(O_2CCH_3)_4$, the Mo−O bond lengths (2.11−2.14 Å)[19] are

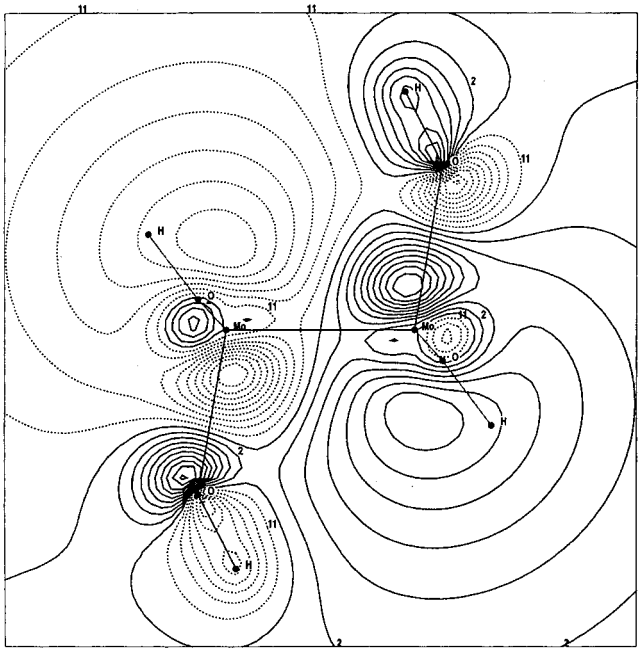

Figure 8. Contour plot of the SLUMO drawn in the σ_h plane.

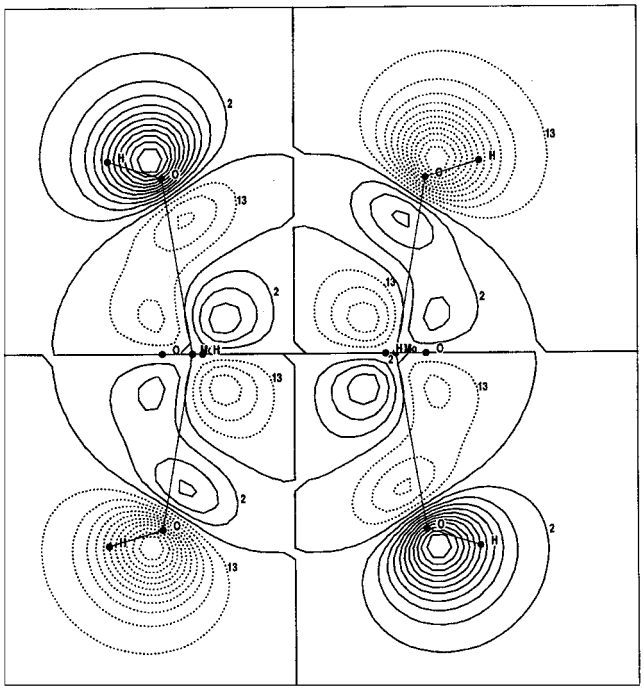

Figure 9. Contour plot of the vacant M−M ($p\pi - p\pi$) π^* molecular orbital.

Table 3. Orbital Energies (eV) of the Frontier MO's of a C_{2h}-$Mo_2(OH)_6$ Molecule as Deduced from the Calculations

SHOMO	−4.50	LUMO	−1.02
HOMO	−2.68	SLUMO	−0.96

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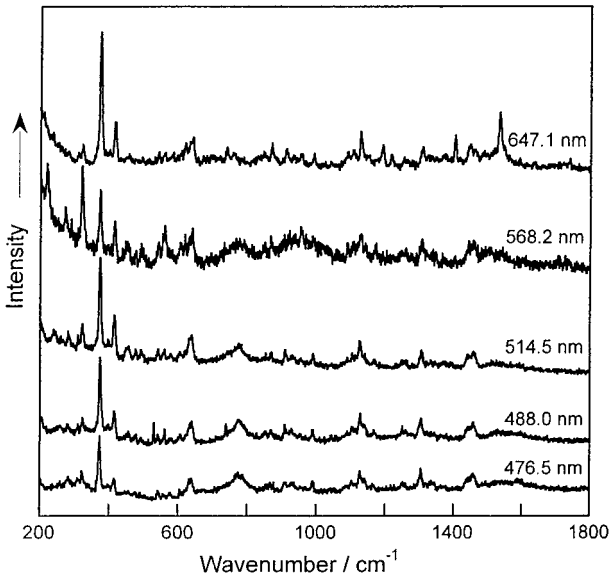

Figure 10. Raman spectra of Mo_2L_2 at various excitation wavelengths.

longer than those for Mo_2L_2 (1.86−2.02 Å), and so the ν(Mo−O) values for the former (301−323 cm^{-1})[17] would be expected to lie below those for the latter. The long Mo−N bond (ca. 2.4 Å) means that the Mo−N stretch should occur at even lower wavenumber, below 300 cm^{-1}. It must be remembered, however, that four of the five Raman-active vibrational modes have the same symmetry and can mutually interact.

Samples of Mo_2L_2 in the form of a mixture with KCl were examined as pressed disks at liquid-nitrogen temperature. Since the complex is blue, we obtained Raman spectra at various wavelengths, and this revealed some fascinating spectral changes. Raman spectra of Mo_2L_2 recorded in KCl at excitation wavelengths ranging from 647.1 to 476.5 nm are shown in Figure 10. The spectra show a number of interesting features. First, five bands are seen between 280 and 414 cm^{-1}. The spectrum recorded at 568.2 nm, near the peak of the electronic band, shows strong enhancement of the 322 cm^{-1} band, lesser enhancement of the 373 and 414 cm^{-1} bands, and the appearance of a strong band at 217 cm^{-1}, possibly arising from a deformation mode. Raman band intensities were measured relative to that of the $\nu_1(a_1)$ band of perchlorate in $KClO_4$ as the internal standard; however, as this matrix for Mo_2L_2 was less thermally stable than that formed in KCl, only qualitative excitation profiles could be obtained. These have been plotted in Figure 11, where it can be seen that there is an approximate correlation with the electronic band profile. The assignments of the Raman bands and the interpretations of the excitation profiles are complicated by both the mixing of the vibrational modes and the mixing of the Mo−Mo and Mo−O orbitals. A tentative assignment is that the highly enhanced 322 cm^{-1} band has a high percentage of Mo−Mo character while the less enhanced 373 and 414 cm^{-1} bands are best described as arising from A_g Mo−O stretches with some Mo−Mo character. The unenhanced 310 and 280 cm^{-1} bands are then assigned to the B_g Mo−O stretch and the Mo−N stretch, respectively. These tentative assignments, along with a tabulation of the observed band maxima, are given in Table 4.

These spectra are notable for an extensive series of combination bands between 490 and 1500 cm^{-1}. These are present even at the longest wavelength used, 647.1 nm, on the low-energy edge of the HOMO−LUMO band centered at 580 nm. It is interesting to note that most of these combination bands involve the mode at 217 cm^{-1} (probably a deformation mode) rather than the metal−metal stretch, as is often the case for multiply bonded metal−metal complexes. This implies that the geometric change on electronic excitation involves changes in both Mo−O(N) bond lengths and the Mo−Mo−O(N) angles (ca 99°), leading to a change of geometry around the ligand "cage", with only a small change in the Mo−Mo bond length. This is consistent with the mixing of Mo−Mo and Mo−O orbitals indicated by the calculations.

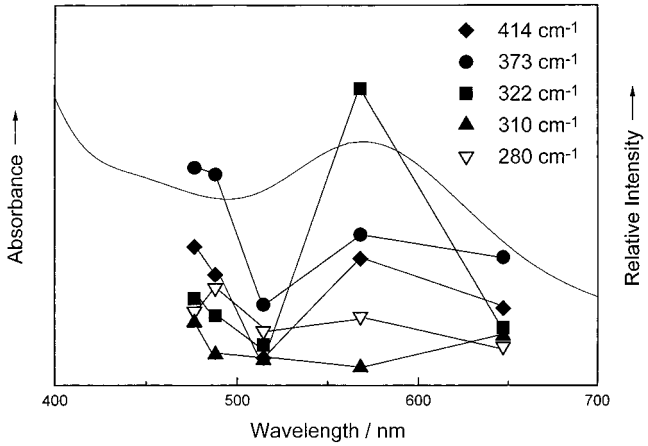

Figure 11. Excitation profiles of the Raman bands of Mo_2L_2 at 414, 373, 322, 310, and 280 cm^{-1}, together with the electronic spectrum.

Concluding Remarks

The use of the (*S*,*S*,*S*)-triisopropanolamine to generate the dimolybdenum bis(triolate) Mo_2L_2 has, by virtue of its coordination requirements, yielded an unusual d^3-d^3 compound. Though the M−M bond is not directly bridged by oxygen atoms, the geometry of the O_6N_2 unit imposes an unusual electronic configuration on the Mo_2^{6+} unit. The degeneracy of the e molecular orbitals (π, δ, π^*, δ^*) is removed, and extensive mixing of M−M and M−O bonding is evident from the calculations. Nevertheless, the d^3-d^3 interaction can be said to give rise to a formal M−M triple bond of the type $\sigma^2\pi_b^2\pi_a^2$. The LUMO is clearly predicted by the calculations to have M−M π^* character, while the SLUMO has M−M σ^* character with considerable admixture of metal sp and oxygen character. The unusual blue color for an M−M triply bonded complex can reasonably be considered to arise from the low-energy singlet−singlet transition, HOMO → LUMO, at 580 nm. The Raman spectra show complex but interesting resonance enhancements as the absorption band at 580 nm is traversed. The Raman band at 322 cm^{-1} can reasonably be stated to have significant Mo−Mo character.

Experimental Section

General Procedures. All syntheses and sample manipulations were carried out under an atmosphere of dry and deoxygenated nitrogen with standard Schlenk and glovebox techniques. Hydrocarbon solvents were distilled under N_2 from Na/benzophenone and stored over 4 Å molecular sieves. Spectra were recorded on a Varian XL-300 (300 MHz) spectrometer in dry and deoxygenated benzene-d_6 or toluene-d_8. All ^1H and ^{13}C NMR chemical shifts are reported in ppm relative to the residual protio impurities or ^{13}C signals of the deuterated solvents. Infrared spectra were obtained from KBr pellets with a Nicolet S10P FT-IR spectrometer.

Chemicals. The preparations of $M_2(NMe_2)_6$ (M = Mo, W) and $M_2(O^tBu)_6$ (M = Mo, W) have been described previously.[9−12] The

(19) Cotton, F. A.; Mester, Z. C.; Webb, T. R. *Acta Crystallogr., Sect. B* **1974**, *30*, 2767.

Table 4. Wavenumbers and Tentative Assignments of Bands in the Raman Spectrum of Mo_2L_2

ν, cm^{-1}	assignment	ν, cm^{-1}	assignment
217[a] s		1088 w	2 × 217 + 280 + 373 = 1087
247 vw, br		1103 w	
280[b] vw	ν(Mo−N)?	1125 m	2 × 217 + 322 + 373 = 1129
310 w	ν(Mo−O)	1143[b] w	
322 m[c]	ν(Mo−Mo)	1167 vw	2 × 217 + 322 + 414 = 1170
373 s	ν(Mo−O)	1188 m	
414 m	ν(Mo−O)	1214 m	2 × 217 + 776 = 1210
454 w		1253 w	
476 w		1305 m	CH_2 wag
493 w	217 + 280 = 497	1318 w	
542 w	217 + 322 = 539	1336 vw	
559 w		1386 vw	3 × 217 + 322 + 414 = 1387
577 vw		1398 m	CH def
635 m	217 +414 = 631 and/or 310 + 322 = 632	1442 w	217 + 454 + 776 = 1447
		1459[b] w	217 + 476 + 776 = 1469
684 m	310 + 373 = 683	1530 m	CH_3 def
737 w	322 + 414 = 736	1590 vw	
758 vw		2518 vw	
776[b] m, br		2847 w	ν(C−H)
846 w	2 × 217 + 414 = 848	2878 w	ν(C−H)
868 m	217 + 280 + 373 = 870	2891 w	ν(C−H)
910 w	217 + 322 + 373 = 912	2928 m	ν(C−H)
929 vw		2966 m	ν(C−H)
954 w	217 + 322 + 414 = 953	3042 m	ν(C−H)
990 w	217 + 776 = 993		

[a] The intensity designations s, m, w, and vs pertain to 647.1 nm excitation and may be substantially different with other excitations. In particular, the band at 217 cm^{-1} is only seen with 568.2 nm excitation. [b] Bands appearing at 280, 776, 1143 and 1459 cm^{-1} occur 4−7 cm^{-1} lower with 568.2 nm excitation than with 476.5, 488.0, 514.5, and 647.1 nm excitation. The reason for this is not clear. [c] This band is the most intense in the whole spectrum with 568.2 nm excitation.

ligand (*S*,*S*,*S*)-triisopropanolamine was synthesized from (*S*)-propylene oxide and (*S*)-1-amino-2-propanol (Aldrich).[8]

Mo_2L_2 (L = N(CH_2CHMeO^-)$_3$). A reaction mixture of $Mo_2(OBu^t)_6$ (315 mg, 0.50 mmol) and (*S*,*S*,*S*)-triisopropanolamine (195 mg, 1.0 mmol) in 20 dm^3 of benzene was stirred at room temperature for 2 h to obtain a blue solution. The volatile components were removed in vacuo, and the residue was suspended in hexane to give a blue precipitate, Mo_2L_2, which was collected and dried in vacuo (241 mg, yield 83%). The compound Mo_2L_2 could also be synthesized from a reaction mixture of $Mo_2(NMe_2)_6$ and (*S*,*S*,*S*)-triisopropanolamine in a similar yield. Crystals of $Mo_2L_2 \cdot 2C_6H_6$ suitable for X-ray analysis were obtained by slow evaporation of a benzene solution. Anal. Calcd (found) for $C_{30}H_{48}O_6N_2Mo_2$: C, 49.73 (49.65); H, 6.68 (6.60); N, 3.87 (3.96). ^{1}H NMR (300 MHz, 20 °C, benzene-d_6): C*H*, δ 5.42 (m, 2H), δ 5.27 (m, 2H), δ 3.51 (m, 2H); CH_2, δ 2.85 (m, 2H), δ 2.56 (m, 2H), δ 2.07 (m, 2H), δ 1.78 (m, 2H), δ 1.67 (m, 2H), δ 1.44 (m, 2H); CH_3, δ 1.36 (d, 6H), δ 1.29 (d, 6H), δ 1.18 (d, 6H). ^{13}C{^{1}H} NMR (125 MHz, 20 °C, benzene-d_6): *C*H, δ 75.11, δ 73.86, δ 70.52; *C*H_2, δ 69.25, δ 68.38, δ 65.12; *C*H_3, δ 22.82, δ 23.42, δ 21.47.

W_2L_2 (L = N(CH_2CHMeO^-)$_3$). A reaction mixture of $W_2(OBu^t)_6$ (402 mg, 0.50 mmol) and (*S*,*S*,*S*)-triisopropanolamine (192 mg, 1.0 mmol) in 15 dm^3 of benzene was stirred at room temperature for 4 h to obtain a blue solution. The volatile components were removed in vacuo, and the residue was washed with hexane to give a green powder, W_2L_2, which was dried in vacuo (213 mg, yield 67%). The compound W_2L_2 could also be synthesized from a reaction mixture of $W_2(NMe_2)_6$ and (*S*,*S*,*S*)-triisopropanolamine in a similar yield. ^{1}H NMR (300 MHz, 20 °C, benzene-d_6): C*H*, δ 5.54 (m, 2H), δ 5.33 (m, 2H), δ 3.43 (m, 2H); CH_2, δ 2.96 (m, 2H), δ 2.31 (m, 2H), δ 2.19 (m, 2H), δ 1.79 (m, 2H), δ 1.60 (m, 2H), δ 1.44 (m, 2H); CH_3, δ 1.39 (d, 2H), δ 1.24 (d, 6H), δ 1.17 (d, 6H). ^{13}C{^{1}H} NMR (125 MHz, 20 °C, benzene-d_6): *C*H, δ 76.88, δ 72.49, δ 72.27; *C*H_2, δ 69.48, δ 68.51, δ 66.25; *C*H_3, δ 23.81, δ 23.32, δ 21.14.

Crystallographic Studies. General operating procedures and a list of programs have been given previously,[20] and a summary of the crystal data is given in Table 5. Bright blue crystals were formed on the sides of the flask in the crystallizing medium. Several different crystals were examined before a suitable sample was obtained because the crystals tended to lose solvent fairly rapidly. A systematic search of a limited hemisphere of reciprocal space was used to determine that the crystal possessed monoclinic symmetry with systematic absences corresponding to a *C*-centered cell but no other extinctions. Subsequent solution and refinement of the structure confirmed the noncentrosymmetric space group *C*2 as the proper choice. The data were collected using a standard moving crystal−moving detector technique with fixed backgrounds at each extreme of the scan. The data were then corrected for Lorentz and polarization effects, and equivalent reflections were averaged.

Table 5. Summary of Crystal Data

empirical formula	$C_{30}H_{48}Mo_2N_2O_6$
color of crystal	blue
crystal system; space group	monoclinic: *C*2
a, Å	17.389(6)
b, Å	10.843(3)
c, Å	10.463(3)
α, deg	90.00(0)
β, deg	125.28(1)
γ, deg	90.00(0)
V, Å^3	1610.45
Z, molecules/cell	2
d_{calcd}, g dm^{-3}	1.494
M_r	724.60
linear abs coeff, cm^{-1}	8.195
R(*F*)[a]	0.051
$R_w(F)$[b]	0.048

[a] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w(F) = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$. $R_w(F) = [\sum w(|F_o| - |F_c|)^2/(N_{observns} - N_{variables})]^{1/2}$.

The structure was finally solved using direct methods (SHELX) and Fourier techniques. Because of the disorder present, some difficulty was encountered during the solution of the structure. While two Mo atom occupancies (Mo(1), 48% occupancy; Mo(2), 45% occupancy) dominate, the third (Mo(3), 6% occupancy) was initially thought to involve a disordered part of the ligand. When the nature of the disorder was finally resolved, the structure slowly converged. As shown for the thermal ellipsoids, there is probably a slight disorder in the ligands. All hydrogen atoms were placed in fixed idealized positions for the final cycles of the refinement. The structure can be described as

(20) Chisholm, M. H.; Folting, K.; Huffman, J. C.; Kirkpatrick, C. C. *Inorg. Chem.* **1984**, *23*, 1021.

possess a pseudocubic coordination environment consisting of two nitrogen and six oxygen atoms, with the disordered Mo atoms in each face of the cube, and the six O atoms forming an octahedron. The molecule lies on the 2-fold axis of the cell, and a benzene solvent molecule is present as well.

The absolute structure was determined by examination of the residuals for the two enantiomers. A final difference Fourier map was featureless, with a maximum peak intensity of 0.79 e/Å^3.

Raman Spectra. Raman spectra were recorded for the sample pressed into an approximately 50:50 disk with KCl and held in a purpose-built cryostat cooled with liquid nitrogen. Spectra were excited at wavelengths between 476.5 and 647.1 nm with radiation from Coherent Innova 70 Ar^+ and 301 Kr^+ lasers. The power at the sample ranged from 50 to 110 mW, depending on the laser line. The entrance slits of the Spex 1401 monochromator were set to give a spectral bandwidth of 4 cm^{-1} for each excitation wavelength. Band wavenumbers were calibrated by superimposing neon emission lines on the Raman spectra to give an estimated accuracy of ±1 cm^{-1}.

The excitation profile was recorded at the wavelengths used for Raman excitation using a disk consisting of Mo_2L_2, $KClO_4$, and KCl in the approximate proportion 2:1:1. Due to problems of sample burning and increased Rayleigh scattering, it was only possible to record excitation profiles of the 414 and 373 cm^{-1} bands with this disk. Excitation profiles of the other bands were calculated from the relative intensities of the 373 and 414 cm^{-1} bands in the appropriate KCl spectra. All spectra were corrected for the wavelength dependence of the spectrometer response.

Computational Procedures. The Mo−Mo and Mo−O distances and Mo−Mo−O angles used in the initial calculations were 2.19 and 1.89 Å and 103°, respectively, which are typical for $Mo_2(OR)_6$ compounds.[21] Calculations on $Mo_2(OH)_6(NH_3)_2$ were modeled on the observed structural parameters observed for the Mo_2L_2 complex reported here, where O−H was substituted for O−C and NH_3 was substituted for $N(CH_2)_3$. The data presented in this work pertaining to the idealized C_{2h}-$Mo_2(OH)_6$ molecule differed only qualitatively from those obtained for $Mo_2(OH)_6(NH_3)_2$ and allowed a ready comparison with those found for the idealized D_{3d}-$Mo_2(OH)_6$ molecule. The B3LPY DFT calculations employed Gaussian 98.[22]

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Supporting Information Available: An X-ray crystallographic file, in CIF format, for the Mo_2L_2 complex. This material is available free of charge via the Internet at http://pubs.acs.org.

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