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Synthesis and Structural Characterization of the Trinuclear Mixed-Valence Complex $[\{(\text{tiptacn})\text{Mo}^{\text{V}}\text{O}(\mu\text{-O})_2\}_2\text{Mo}^{\text{IV}}(\text{bpy})](\text{PF}_6)_2\cdot 0.25\text{CH}_3\text{NO}_2$ (tiptacn = 1,4,7-Tris(2-propyl)-1,4,7-triazacyclononane)

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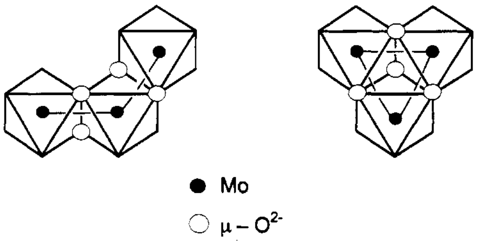
Reaction of $(\text{tiptacn})\text{Mo}^{\text{III}}\text{Cl}_3$ with 2,2′-bipyridine in aqueous methanol in the presence of air yields after addition of NaPF_6 deep red crystals of $[\{(\text{tiptacn})\text{Mo}^{\text{V}}\text{O}(\mu\text{-O})_2\}_2\text{Mo}^{\text{IV}}(\text{bpy})](\text{PF}_6)_2\cdot 0.25\text{CH}_3\text{NO}_2$ (**1**) where tiptacn represents the tridentate amine 1,4,7-tris(2-propyl)-1,4,7-triazacyclononane. Results of the structure determination on **1** [monoclinic space group $C2/c$, $a = 15.158(7)$ Å, $b = 22.135(8)$ Å, $c = 20.04(1)$ Å, $\beta = 109.84(4)°$, $V = 6324.8(15)$ Å^3, $Z = 4$] have shown that the cation is trinuclear with two terminal $(\text{tiptacn})\text{Mo}^{\text{V}}\text{O}(\mu\text{-O})_2$ units and a central $\text{Mo}^{\text{IV}}(\text{bpy})$ unit. Two short Mo^{V}–Mo^{IV} distances at 2.581(2) Å are typical for Mo–Mo single bonds. **1** is diamagnetic.

Introduction

As Young has recently commented in his excellent review article on mixed-valence compounds of the early transition metals, molybdenum is the element par exellence in terms of mixed-valence chemistry.[2] In molecular oxomolybdenum chemistry, a number of mixed-valence dinuclear species containing $\text{Mo}^{\text{V}}\text{Mo}^{\text{VI}}$,[3] $\text{Mo}^{\text{IV}}\text{Mo}^{\text{VI}}$,[4] and $\text{Mo}^{\text{III}}\text{Mo}^{\text{VI}}$ [5] have been structually characterized. A complex $[\text{Mo}^{\text{IV}}\text{Mo}^{\text{V}}\text{O}_2(\text{R}_2\text{dtc})_4]\text{PF}_6$ has been described, but the structure has not been reported.[6] In contrast, mixed-valence trinuclear oxomolybdenum species are far less well characterized.[2] Some of the complexes containing a $[\text{Mo}^{\text{IV}}{}_3(\mu_3\text{-O})(\mu_2\text{-O})_3]^{4+}$ core depicted in Chart I are known to undergo an electrochemical two-electron reduction which is accompanied by protonation of the μ-oxo ligands, yielding diamagnetic $\text{Mo}^{\text{III}}{}_2\text{Mo}^{\text{IV}}$ species.[7] None of these have been isolated and characterized by X-ray crystallography to date.

Complexes with the $[\text{Mo}^{\text{IV}}{}_3\text{O}_4]^{4+}$ core contain an equilateral triangular arrangement of three molybdenum(IV) ions which are bound to each other by Mo–Mo single bonds (Mo–Mo ≈ 2.50 Å).[8] Formally, a metal-centered two-electron *oxidation* of this core accompanied by a slight rearrangement of the oxo bridges would produce a $\text{Mo}^{\text{V}}{}_2\text{Mo}^{\text{IV}}$ trinuclear species containing a $[\text{Mo}^{\text{V}}{}_2\text{Mo}^{\text{IV}}(\mu_2\text{-O})_4]^{6+}$ core (Chart I, left-hand side) where one Mo–Mo bond of the $[\text{Mo}^{\text{IV}}{}_3\text{O}_4]^{4+}$ unit has been removed. Complexes containing this core have not been reported to date. We present here the first example of this kind. We have recently begun to explore the coordination chemistry of the bulky tridentate amine 1,4,7-tris(2-propyl)-1,4,7-triazacyclononane (tiptacn) with molybdenum.[9] This ligand reacts readily with Mo(CO)_6 to form yellow, air-stable $(\text{tiptacn})\text{Mo(CO)}_3$, the structure of which has been determined. Exhaustive decarbonylation of this complex with thionyl chloride affords in excellent yields monomeric $(\text{tiptacn})\text{Mo}^{\text{III}}\text{Cl}_3$, which proved to be a useful starting material for the synthesis of di- and trinuclear oxomolybdenum complexes. Here we describe the preparation and crystal structure of the mixed-valence complex $[\{(\text{tiptacn})\text{Mo}^{\text{V}}\text{O}(\mu\text{-O})_2\}_2\text{Mo}^{\text{IV}}(\text{bpy})](\text{PF}_6)_2$ (**1**).

Chart I. Core Structures of Mo_3O_4



Experimental Section

The ligand 1,4,7-tris(2-propyl)-1,4,7-triazacyclononane and the complex $(\text{tiptacn})\text{MoCl}_3$ were prepared as described previously.[9]

Preparation of $[\{(\text{tiptacn})\text{MoO}(\mu\text{-O})_2\}_2\text{Mo(bpy)}](\text{PF}_6)_2$ (1). To a suspension of $(\text{tiptacn})\text{MoCl}_3$ (0.46 g; 1.0 mmol) in methanol (50 mL) was added 2,2′-bipyridine (0.50 g) in the presence of air. The mixture was heated to reflux for 24 h. The then deep red solution was filtered in order to remove unreacted $(\text{tiptacn})\text{MoCl}_3$. A saturated methanolic solution of NaPF_6 (5 mL) was then added, whereupon dark red microcrystals of **1** precipitated, which were filtered off, washed with diethyl ether, and air-dried. Yield: 0.30 g; 67%. Crystals suitable for X-ray crystallography were grown from a mesitylene/nitromethane mixture. They contain 0.25–0.50 equiv of CH_3NO_2 per formula unit. Anal. Calcd for $[\text{C}_{40}\text{H}_{74}\text{N}_8\text{Mo}_3\text{O}_6\text{P}_2\text{F}_{12}]\cdot 0.5\text{CH}_3\text{NO}_2$: C, 35.47; H, 5.55; N, 8.68. Found: C, 35.3; H, 5.5; N, 9.1.

X-ray Structure Determination. Intensities and lattice parameters of a dark red crystal of **1** were measured on a Syntex R3 diffractometer at ambient temperature by using Mo Kα X-radiation. Crystal parameters and details of the data collection are given in Table I. An empirical absorption correction (ψ-scans of seven reflections) was carried out. The structure was solved with conventional Patterson and difference Fourier methods by using the SHELXTL-PLUS (PC version) program package (Siemens). The function minimized during full-matrix least-squares refinement was $\sum w(|F_o|-|F_c|)^2$, where $w = \sigma(F)^{-2}$. Neutral-atom scattering

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Table I. Crystallographic Data for **1**

chem formula $[C_{40}H_{74}N_8Mo_3O_6P_2F_{12}]\cdot0.25CH_3NO_2$	fw 1348.8
	space group $C2/c$ (No. 15)
$a = 15.158(7)$ Å	$T = 298$ K
$b = 22.135(8)$ Å	$\lambda = 0.710\ 73$ Å
$c = 20.04(1)$ Å	$\rho_{calcd} = 1.43$ g/cm^3
$\beta = 109.84(4)$ deg	$\mu = 0.70$ mm^{-1}
$V = 6324.8(15)$ Å^3	$R^a = 0.058$ (obsd data)
$Z = 4$	$R_w{}^b = 0.050$ (obsd data)

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

Table II. Atomic Coordinates ($\times10^4$) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3)

atom	x	y	z	U(eq)[a]
P1	1133(2)	5732(1)	−739(1)	70(1)
F11	499(4)	5774(3)	−1537(3)	135(4)
F12	1906(5)	6087(4)	−899(3)	158(4)
F13	1761(4)	5702(3)	67(3)	115(3)
F14	1556(6)	5146(4)	−889(4)	187(5)
F15	357(6)	5378(5)	−590(5)	207(6)
F16	673(6)	6315(3)	−581(3)	167(5)
Mo1	3609(1)	6413(1)	−3054(1)	37(1)
Mo2	5000	7137(1)	−2500	34(1)
C1	4854(5)	8502(3)	−2187(4)	49(3)
C2	4789(6)	9014(4)	−1805(6)	76(5)
C3	4541(7)	8961(5)	−1209(6)	85(5)
C4	4372(7)	8398(5)	−994(5)	80(5)
C5	4464(6)	7905(4)	−1388(5)	61(4)
N4	4676(4)	7955(3)	−1974(3)	46(3)
O1	4268(3)	5854(2)	−3204(2)	44(2)
O2	4171(3)	6728(2)	−2097(2)	38(2)
O3	3911(3)	7141(2)	−3424(2)	40(2)
N1	2790(4)	5564(3)	−2830(3)	52(3)
N2	2179(4)	6818(3)	−2890(3)	51(3)
N3	2467(5)	6297(3)	−4138(3)	56(3)
C11	1939(5)	5733(4)	−2636(5)	62(4)
C12	1985(6)	6386(4)	−2386(5)	60(4)
C13	1401(6)	6818(4)	−3589(5)	66(4)
C14	1774(6)	6796(4)	−4198(4)	62(4)
C15	1983(6)	5703(4)	−4155(4)	67(4)
C16	2492(6)	5279(3)	−3550(5)	61(4)
C17	3456(6)	5143(3)	−2282(5)	63(4)
C18	2288(6)	7429(3)	−2523(5)	59(4)
C19	2859(7)	6364(5)	−4747(4)	72(4)
C20	3033(7)	4505(3)	−2281(5)	97(6)
C21	3779(6)	5416(4)	−1538(4)	66(4)
C22	1477(7)	7609(4)	−2267(5)	95(6)
C23	2436(6)	7925(3)	−2990(5)	72(4)
C24	2059(7)	6418(5)	−5468(5)	104(6)
C25	3538(7)	5879(5)	−4770(5)	106(6)
C31	595(37)	1828(24)	4590(29)	118(18)
C32	155(33)	2026(20)	4780(23)	82(15)
C33	184(30)	1637(18)	4121(23)	99(13)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

factors and anomalous dispersion corrections were taken from ref 10. The positions of H atoms were calculated (C–H = 0.96 Å; riding model for CH_3 groups) and included in the refinement with a common isotropic thermal parameter $U = 0.080$ Å^2. The C, N, and O atoms of the nitromethane solvent molecule were found to be highly disordered, and no chemically reasonable model has been found. Atoms C31, C32, and C33 were refined as carbon atoms. Treatment of their respective occupancy factors as variables yielded a value of 0.25. Thus the crystal probably lost a small amount of CH_3NO_2 during the intensity collection although the intensity of the three reference reflections measured after every 200 reflections did not show a systematic decrease. Atom coordinates are summarized in Table II.

Results and Discussion

Synthesis and Spectroscopic Characterization. The bulky tridentate macrocyclic amine 1,4,7-tris(2-propyl)-1,4,7-triazacyclononane (tiptacn) reacts with $Mo(CO)_6$ in refluxing mesitylene, affording yellow, air-stable (tiptacn) $Mo(CO)_3$. Exhaustive decarbonylation of this complex with thionyl chloride in refluxing CCl_4 gives yellow (tiptacn) $Mo^{III}Cl_3$ in ≈75% yield.[9] Reaction of (tiptacn)$MoCl_3$ with 2,2′-bipyridine in refluxing methanol containing ≈5% water in the presence of air affords a clear deep red solution. Upon addition of $NaPF_6$, dark red microcrystals of $[\{(tiptacn)MoO(\mu\text{-}O)_2\}_2Mo(bpy)](PF_6)_2$ (**1**) are obtained in 67% yield based on (tiptacn) $MoCl_3$. Diamagnetic **1** is soluble in polar organic solvents and in water; it is stable toward oxygen.

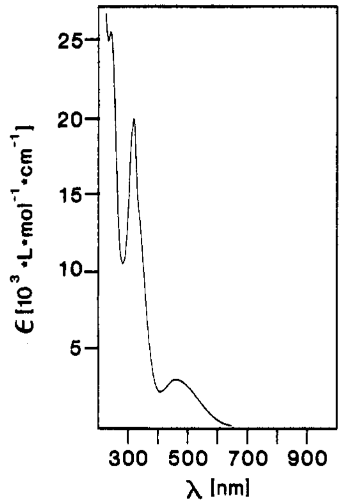

Figure 1. Electronic spectrum of **1** in acetonitrile at 20 °C.

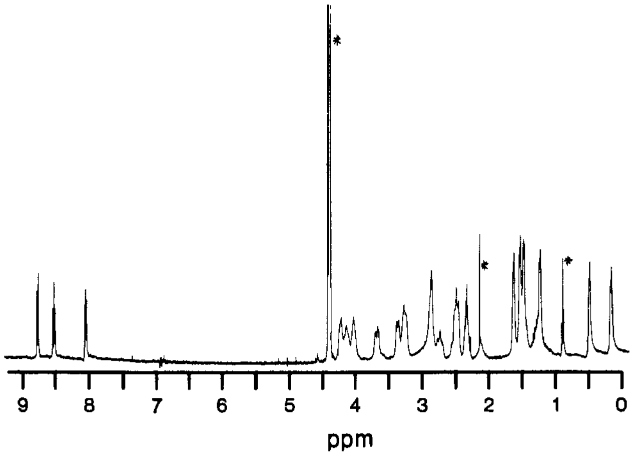

Figure 2. 400-MHz ^1H NMR spectrum of **1** in CD_3NO_2. Solvent impurities of CH_3NO_2, acetone, water, and diethyl ether (left to right) are marked by an asterisks.

In the infrared spectrum of **1** (KBr disk) strong bands at 956 and 762 cm^{-1} indicate the presence of terminal Mo═O and bridging M—O—Mo entities, respectively. Figure 1 shows the electronic spectrum of **1** in acetonitrile. λ_{max}, nm (ϵ, L mol^{-1} cm^{-1}): 455 (3.1×10^3), 313 (19.6×10^3), 237 (25.0×10^3). From a single-crystal X-ray structure determination (see below), it follows that **1** contains the trinuclear mixed-valence dication $[\{(tiptacn)Mo^VO(\mu\text{-}O)_2\}_2Mo^{IV}(bpy)]^{2+}$.

Figure 2 shows the 400-MHz ^1H NMR spectrum of **1** in CD_3NO_2. Resonances due to coordinated 2,2′-bipyridine are observed at $\delta = 7.9$–10.1 whereas in the range $\delta = 2.0$–4.5 a series of complex signals due to methylene and methine protons of the coordinated tiptacn ligands is detected. The proton signals of the six methyl groups of the three 2-propyl substituents of the coordinated macrocycle give rise to six singlets in the range $\delta = 0.2$–1.6. This clearly indicates that all six methyl groups are magnetically inequivalent. Two signals at $\delta = 0.2$ and 0.5 display remarkable high-field shifts. As is clearly seen in the crystal

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(10) *International Tables for X-ray Crystallography*; Kynoch: Brimingham, England, 1974; Vol. IV, pp 99, 149.

Table III. Compilation of ^{95}Mo NMR Data for Oxo-Bridged Di- and Trinuclear Molybdenum(IV) and -(V) Complexes[a]

complex	solvent	T, °C	δ ($W_{1/2}$),[b] ppm (Hz)	ref
$Mo^{IV}_3O_4(aq)^{4+}$	HMS	50	990 (620)	8c
$Na_4[Mo^{IV}_3O_4)_2(edta)_3]\cdot 14H_2O$	D_2O	50	1083 (100)	8c
$Mo^{V}_2O_4(aq)^{2+}$	HMS	50	542 (300)	8c
syn-$[(tacd)_2Mo^{V}_2O_4](ClO_4)_2\cdot 2H_2O$	CH_3CN	70	547 (700)	16
syn-$[(tacn)_2Mo^{V}_2O_4]I_2$	H_2O	70	586 (250)	16
1	CH_3CN	70	988 (465) 554 (620)	this work

[a] Abbrevations: HMS = methanesulfonic acid, edta = ethylenediaminetetraacetate, tacd = 1,5,9-triazacyclododecane, tacn = 1,4,7-triazacyclononane. [b] Chemical shift and in parentheses peak half-width at half-height.

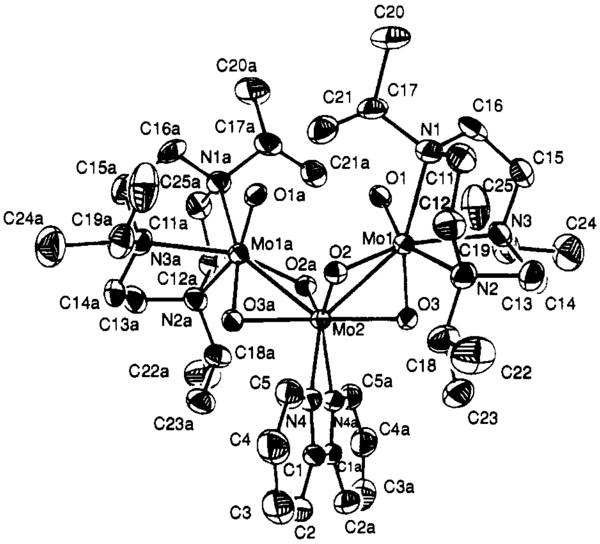

Figure 3. Structure and atom-labeling scheme of the trinuclear dication in crystals of **1**.

structure of **1** (Figure 3), four methyl groups of two 2-propyl substituents (C22, C23 and C22A, C23A) are in close proximity to the aromatic rings of the coordinated 2,2′-bipyridine ligand at Mo2. The observed high-field shifts of the methyl proton signals are then due to the influence of the anisotropy cone originating from the bpy ligand. Since the distance of these protons from the aromatic rings is in the range 3.2–3.8 Å, one can estimate[11] that the high-field shifts are of the order of 1.0 and 1.4 ppm when the signals of the other four methyl groups (δ = 1.3–1.7) represent uninfluenced reference values. We conclude that the solid-state structure is retained in solution.

The ^{95}Mo NMR spectrum of **1** recorded in CH_3CN at 70 °C (2.0 M Na_2MoO_4 in D_2O as external standard) shows two signals at δ = 988 and 554. As may be rationalized from the brief compilation in Table III of data for metal–metal-bonded oxo-bridged di-trinuclear molybdenum(IV) and -(V) species, the observed chemical shift of these signals is in the typical narrow range observed for these oxidation states:[8c,12] Mo(IV), 990–1200 ppm; Mo(V), 500–650 ppm. Thus ^{95}Mo NMR spectroscopy supports the assignment of these oxidation states in **1**, which is a mixed-valence $Mo^{V}_2Mo^{IV}$ species.

The cyclic voltammogram of **1** recorded in 0.10 M tetra-*n*-butylammonium hexafluorophosphate–acetonitrile solution at a glassy carbon working electrode and a scan rate of 50 mV/s displays a quasi-reversible one-electron reduction process at −1.74 V vs the ferrocenium (Fc^+)/ferrocene (Fc) couple and an irreversible process at −2.10 V vs Fc^+/Fc.

Crystal Structure of 1. Crystals of **1** consist of trinuclear dications $[\{(tiptacn)MoO(\mu\text{-}O)_2\}_2Mo(bpy)]^{2+}$, hexafluorophosphate anions, and disordered solvent molecules of nitromethane.

Table IV. Selected Bond Distances and Angles for **1**

	Bond Distances (Å)		
Mo1–O1	1.681(5)	Mo2–N4	2.232(7)
Mo1–O2	1.945(4)	Mo2–O2	1.934(5)
Mo1–O3	1.894(5)	Mo2–O3	2.019(4)
Mo1–N1	2.377(7)	Mo1–Mo2	2.581(2)
Mo1–N2	2.468(7)		
Mo1–N3	2.286(6)		
	Bond Angles (deg)		
O1–Mo1–O2	110.6(2)	N1–Mo1–N2	73.9(2)
O1–Mo1–O3	108.7(2)	N1–Mo1–N3	79.3(2)
O2–Mo1–O3	89.9(2)	N2–Mo1–N3	75.6(2)
N1–Mo1–O3	163.3(2)	O2–Mo2–O3	86.6(2)
N2–Mo1–O1	153.3(2)	O3–Mo2–O3A	179.5(3)
N3–Mo1–O2	156.1(2)	O2–Mo2–O2A	124.2(3)
Mo1–Mo2–Mo1A	103.2(1)	N4–Mo2–N4A	71.5(4)
Mo1–O2–Mo2	83.4(2)	Mo1–O3–Mo2	82.5(2)
N4–Mo2–O2	84.5(2)	O2–Mo2–N4A	148.8(2)
N4–Mo2–O3	100.8(2)	O2–Mo2–O2A	124.2(3)
N4–Mo2–O2A	148.8(2)	O2–Mo2–O3A	93.7(2)
O3–Mo2–N4A	78.8(2)		
O3–Mo2–O2A	93.7(2)		

Table IV summarizes important bond lengths and angles; Figure 3 shows the structure of the dication and gives the atom-labeling scheme.

The dication possesses crystallographically imposed C_2 symmetry. The overall structure may be viewed as an assembly of three edge-sharing octahedra held together by four oxo bridges as is depicted in Chart I (left-hand side). The angle Mo1–Mo2–Mo1a at 103.2(1)° is smaller than the value of 120° expected for a regular arrangement. This assembly is to be compared with the more densely packed structurally well-characterized $[Mo^{IV}_3O_4]^{4+}$ core (Chart I; right-hand side), where the Mo–Mo–Mo angles are 60°.

The coordination sphere of the two identical outer molybdenum ions is composed of a facially bound tridentate amine ligand and a terminal and two bridging oxo groups. That of the central molybdenum ion consists of a bidentate 2,2′-bipyridine ligand and four bridging oxo ligands. The geometry is severely distorted octahedral around all three molybdenum ions.

The two identical four-membered $Mo_2(\mu\text{-}O)_2$ rings are puckered and asymmetric with regard to the fact that the Mo–O_{oxo} distances are not equivalent. This asymmetry of the Mo_2O_2 rings may be rationalized by considering the ligand geometry at the central molybdenum ion Mo2 (Figure 3). The oxo bridges O3 and O3A are in trans positions with respect to each other, whereas O2 and O2A are in cis positions relative to each other and in trans positions relative to coordinated nitrogen donor atoms of 2,2′-bipyridine (N4, N4A). Oxo ligands are in general strong π-donors,[13] contrasting in this respect with the nitrogen atoms of coordinated bpy, which are weak π-acceptors. When two π-donors are in trans positions in an octahedral complex, a weakening (elongation) of these bonds is observed. On the other hand, if a π-acceptor ligand is positioned trans with respect to an oxo π-donor, the Mo–O bond is strengthened (shorter). Thus the bond distances

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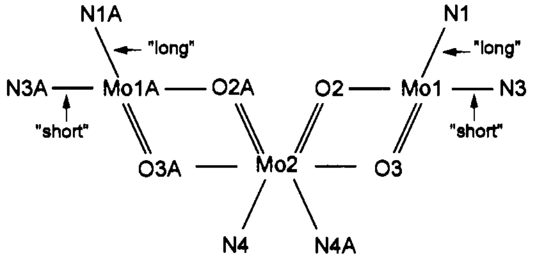
Mo2–O3 and Mo2–O2 differ by 0.085 Å, the former being the longer. This effect is then transmitted onto the Mo1–O3 and Mo1–O2 bond lengths. Since O3 is the slightly stronger π-donor and Mo1 (Mo(V), d^1) is a good π-acceptor, the resulting Mo1–O3 bond is short (1.894(5) Å). Concomittantly, O2 is the weaker π-donor and, consequently, the Mo1–O2 distance is relatively longer (1.945(5) Å). This situation may be depicted by the resonance structure shown in I.



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This alternating series of weak and strong structural trans influences is clearly supported by other structural features. The Mo1–N1 bond in trans position to the shorter Mo1–O3 bond is longer than the corresponding Mo1–N3 bond, which is trans with respect to the weaker Mo1–O2 bond. Note that the nitrogen atoms of the macrocyclic amine are pure σ-donors whereas those of 2,2′-bipyridine are weak π-acceptors. Consequently, the Mo2–N4 and Mo2–N4A bonds are the shortest Mo–N bonds in the trinuclear dication.

Metrical details of the $N_3MoO(\mu\text{-}O)_2$ coordination spheres in 1 are similar to those reported for the symmetrical dinuclear dimolybdenum(V) complex *syn*-$[(tacn)_2Mo^V_2(O)_2(\mu\text{-}O)_2]^{2+}$ where tacn represents 1,4,7-triazacyclononane.[14] The terminal oxo group exerts a pronounced structural trans influence on the trans Mo–N bond. The Mo1–N2 distance is significantly longer than the two Mo1–N bond lengths in cis position to this oxo group.

An important feature of the structure of 1 is the observation of two short Mo–Mo distances at 2.581(2) Å. Simple charge considerations imply that two of the molybdenum ions in 1 have a formal oxidation state +V (d^1) whereas the third must have +IV (d^2). The O–Mo–O angles of the $Mo_2(\mu\text{-}O)_2$ rings are obtuse, and the Mo–O–Mo angles are acute. This, together with the observed diamagnetism of 1, indicates the presence of two Mo–Mo single bonds. Overlap of each of the degenerate half-occupied d_{xz} and d_{yz} orbitals on the Mo(IV) center (z along trans O–Mo–O direction, x and y along other Mo–O bonds) with the respective HOMO perpendicular to Mo(V)=O of a Mo(V) center permits the formation of the two metal–metal single bonds. The Mo–Mo distances in diamagnetic dimolybdenum(V) complexes containing the $[Mo^V_2(\mu\text{-}O)_2(O)_2]^{2+}$ core and in trinuclear molybdenum(IV) species with a $[Mo^{IV}_3(\mu_3\text{-}O)(\mu_2\text{-}O)_3]^{4+}$ core are quite similar to those in 1. Thus in *syn*-$[(tacn)_2Mo^V_2(O)_2(\mu\text{-}O)_2]^{2+}$ the Mo–Mo bond length is 2.555(1) Å and in $[(tacn)_3Mo^{IV}_3O_4]^{4+}$ this distance is 2.511(2) Å.[15]

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Supplementary Material Available: Tables giving crystal data and details of the structure determination, bond lengths, bond angles, anisotropic thermal parameters, and hydrogen locations (7 pages). Ordering information is given on any current masthead page.

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