Syntheses and Crystal Structures of Complexes $[L'O(H_2O)V(\mu\text{-}O)WO_2L]Cl(ClO_4)$ and $[L'(acac)Mo^{III}(\mu\text{-}O)Mo^{VI}O_2L'][BPh_4]_2$ (L,L′ = 1,4,7-triazacyclononane and its 1,4,7-trimethyl derivative; acac = pentane-2,4-dionate)[†]

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Reaction of an equimolar mixture of $[VCl_3L']$ and $[WO_3L]\cdot 3H_2O$ in MeOH–water (4:1) in the presence of air affords upon addition of $NaClO_4$ blue $[L'O(H_2O)V^{IV}(\mu\text{-}O)W^{VI}O_2L]Cl(ClO_4)$ **1** (L′ = 1,4,7-trimethyl-1,4,7-triazacyclononane; L = 1,4,7-triazacyclononane). Crystals of **1** are monoclinic, space group $P2_1/c$, with $a = 9.401(8)$, $b = 20.61(1)$, $c = 13.53(1)$ Å, $\beta = 102.47(7)°$, and $Z = 4$. The complex is an asymmetric, heterodinuclear species consisting of vanadyl $VOL'(OH_2)$ and *cis*-$LW^{VI}O_2$ units which are asymmetrically bridged by an oxygen. A suspension of $[Mo^{III}Br_3L']$ and excess of sodium penta-2,4-dionate (acac) in water reacts in the presence of air with formation of the asymmetric mixed-valence species $[L'(acac)Mo^{III}(\mu\text{-}O)Mo^{VI}O_2L']^{2+}$. The bis(tetraphenylborate) salt **2** crystallizes in the monoclinic space group $P2_1/a$ with $a = 18.589(9)$, $b = 18.30(1)$, $c = 20.432(9)$ Å, $\beta = 104.73(4)°$ and $Z = 4$. The $L'Mo^{III}(acac)$ and *cis*-$L'MoO_2$ units are linked by an asymmetric μ-oxo bridge with $Mo^{III}–O_{oxo}$ and $Mo^{VI}–O_{oxo}$ distances of 2.034(4) and 1.808(4) Å, respectively.

Water-soluble, colourless, octahedral neutral complexes $[MO_3L]\cdot 3H_2O$ and $[MO_3L']\cdot 3H_2O$ ($M = Mo^{VI}$ or W^{VI}, L = 1,4,7-triazacyclononane, L′ = 1,4,7-trimethyl-1,4,7-triazacyclononane) are available in good yields *via* exhaustive oxidative decarbonylation reactions of the respective tricarbonyl complexes $[M(CO)_3L]$ or $[M(CO)_3L']$ with H_2O_2 in tetrahydrofuran or *via* the reaction of MoO_3 or WO_3 with the respective cyclic amine in aqueous solution (Scheme 1).[1,2] These *cis*-trioxometal(VI) species are very stable in aqueous and methanolic or ethanolic solution; no ligand dissociation has been observed in contrast to their open-chain analogues $[MO_3(dien)]$[3,4] (dien = diethylenetriamine). It is therefore possible to study the reactivity of the *cis*-trioxometal(VI) fragment. We have recently shown that in non-co-ordinating aqueous acids ($MeSO_3H$, $HClO_4$) one terminal oxo group is reversibly protonated; $[WO_2(OH)L']Br$ has been crystallographically characterized.[2,5] The nucleophilic properties of the *cis*-MO_3 moiety have also been demonstrated by the reaction of $[MO_3L]$ (M = Mo or W) with $[BPh_4]^-$ in aqueous methanesulphonic acid where the adducts $[LO_2M(\mu\text{-}O)BPh_3]$ and $[(WO_3L)_2BPh_2][BPh_4]$ have been isolated and structurally characterized.[6] Finally, $[MO_3L]$ species can act as ligands in weakly co-ordinating solvents (CH_3OH) toward cobalt(II) and iron(III) cations: $[(MoO_3L')_4Co][BPh_4]_2\cdot EtOH$ and $[(MoO_3L')_4Fe][BPh_4]_3\cdot Na[BPh_4]$ have been structurally characterized.[1,6]

As an extension of this work we report the syntheses and crystal structures of the μ-oxo-bridged heterodinuclear complex $[L'O(H_2O)V^{IV}(\mu\text{-}O)W^{VI}O_2L]Cl(ClO_4)$ **1** and of the asymmetric mixed-valence complex $[L'(acac)Mo^{III}(\mu\text{-}O)Mo^{VI}O_2L'][BPh_4]_2$ **2**. The symmetric mixed-valence species $[Mo_2(acac)_2(\mu\text{-}O)L'_2][PF_6]_3$ **3** has also been prepared.

Results

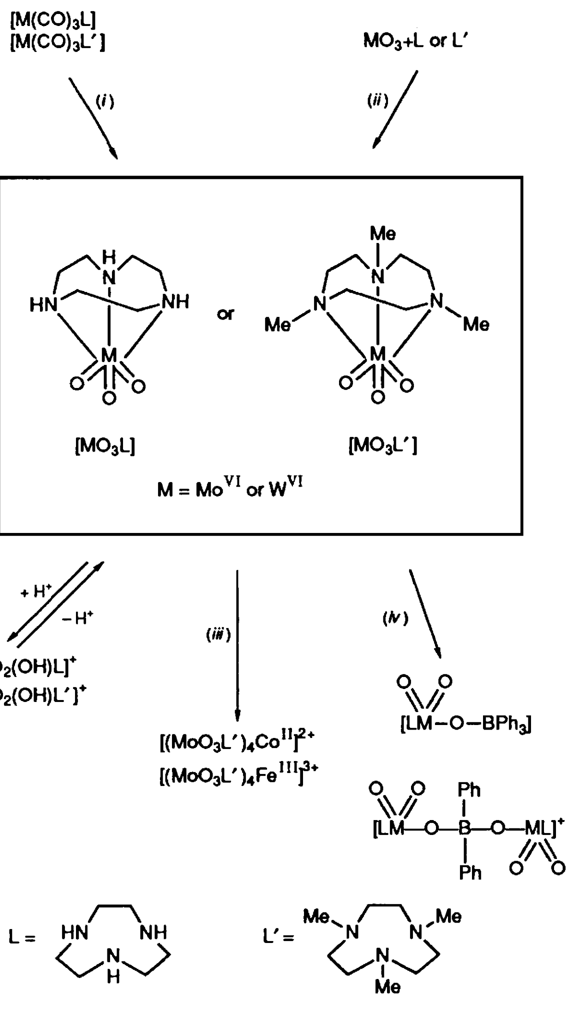
Synthesis of Complexes.—Heating an equimolar mixture of the monomeric complexes $[V^{III}Cl_3L']$ and $[W^{IV}O_3L]\cdot 3H_2O$ in methanol–water (4:1) in the presence of air afforded a clear blue-green solution from which upon addition of $NaClO_4$ a blue-green solid material precipitated. Recrystallization from water gave blue crystals of $[L'O(H_2O)V^{IV}(\mu\text{-}O)W^{VI}O_2L]Cl(ClO_4)$ **1**, soluble in water, MeOH, EtOH and MeCN.

The electronic spectrum of complex **1** in MeCN displays two d–d transitions in the visible at 820 ($\varepsilon = 36$) and 580 nm (30 $dm^3\ mol^{-1}\ cm^{-1}$) which are typical for octahedral vanadyl complexes. The complex is paramagnetic and has a temperature-independent magnetic moment of 1.72 μ_B in the range 81–293 K. The infrared spectrum (KBr disc) displays a series of strong bands in the region 950–750 cm^{-1} which are typical for the different M–O stretching frequencies: $\nu(V{=}O)$ 943, $\nu_{asym}(WO_2)$ 887 and $\nu_{sym}(WO_2)$ 870 cm^{-1}. Bands at 838 and 785 cm^{-1} are assigned to $\nu(V–O)$ and $\nu(W–O)$ stretching frequencies of the V–O–W bridge, respectively.

Fig. 1 shows X-band ESR spectra of complex **1** at 10 K. The solid-state spectrum exhibits a broad signal at $g \approx 2.0$. The frozen-solution spectrum in methanol shows hyperfine structure from which the following spin-Hamiltonian parameters are deduced: $g_\perp = 2.0$ and $g_\parallel = 1.926$ with $A_\perp = 56.1 \times 10^{-4}\ cm^{-1}$ and $A_\parallel = 161.1 \times 10^{-4}\ cm^{-1}$. These values are in good agreement with those found for other monomeric vanadyl complexes of axial symmetry.

[†] Aqua-1κ*O*-μ-oxo-trioxo-1κ*O*,2κ^2*O*-(1,4,7-triazacyclononane-2κ^3*N*)-(1,4,7-trimethyl-1,4,7-triacyclononane-1κ^3*N*)tungsten(VI)vanadium(IV) chloride perchlorate and μ-oxo-dioxo-1κ^2*O*-pentane-2,4-dionato-2κ^2*O*-bis(1,4,7-trimethyl-1,4,7-triazacyclononane)-1κ^3*N*,2κ^3*N*-molybdenum(III)molybdenum(VI)bis(tetraphenylborate).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.



Scheme 1 (*i*) thf, H_2O_2; (*ii*) water; (*iii*) $Co(ClO_4)_2{\cdot}6H_2O$, $Fe(ClO_4)_3{\cdot}9H_2O$, MeOH; (*iv*) BPh_4^-, $MeSO_3H$

When a suspension of [$MoBr_3L'$] (or [$MoCl_3L'$]) and excess of sodium pentane-2,4-dionate (acac) in water is heated to reflux in the presence of air a clear brown solution is obtained. Addition of KPF_6 initiates the precipitation of brown microcrystals of [L′(acac)Mo(μ-O)MoO_2L'][PF_6]$_2$. Single crystals suitable for an X-ray structure determination were grown from a MeOH–MeCN solution of this material to which Na[BPh_4] was added. Brown crystals of [L′(acac)Mo(μ-O)MoO_2L'][BPh_4]$_2$ **2** were obtained.

Interestingly, when the above reaction is carried out under anaerobic conditions under an argon atmosphere and by using [$Mo(O_3SMe)_3L'$]* as starting material, addition of KPF_6 does not lead to the precipitation of **2**. Exposure of this brown solution to air yields within 2 h a blue-violet microcrystalline precipitate of the symmetric mixed-valence dinuclear complex [L′(acac)Mo^{III}(μ-O)Mo^{IV}(acac)L′][PF_6]$_3$ **3**. Further air oxidation of **3** in aqueous solution yields **2**. Reduction of an aqueous solution of **3** with Na[BH_4] yields a clear brown solution which most probably contains the species [Mo^{III}_2(acac)$_2$(μ-O)L'_2]$^{2+}$ since it is possible to reoxidize this species by air to give **3**. We have as yet not been able to isolate a solid material containing this cation.

Complex **2** has a temperature-independent magnetic moment of 3.7 μ_B per formula unit which is typical for an octahedral molybdenum(III) species with d^3 electron configuration. Thus **2** is a $Mo^{III}Mo^{VI}$ mixed-valence species (d^3d^0) with localized valencies. Its electronic spectrum in MeCN exhibits an intense absorption maximum at 386 nm ($\varepsilon = 3.65 \times 10^3$ dm^3 mol^{-1} cm^{-1}) with a shoulder at ≈450 nm. In the infrared spectrum two bands at 821 and 778 cm^{-1} are observed which are tentatively assigned to the ν_{asym} and ν_{sym} stretching frequencies of the *cis*-MoO_2 unit.

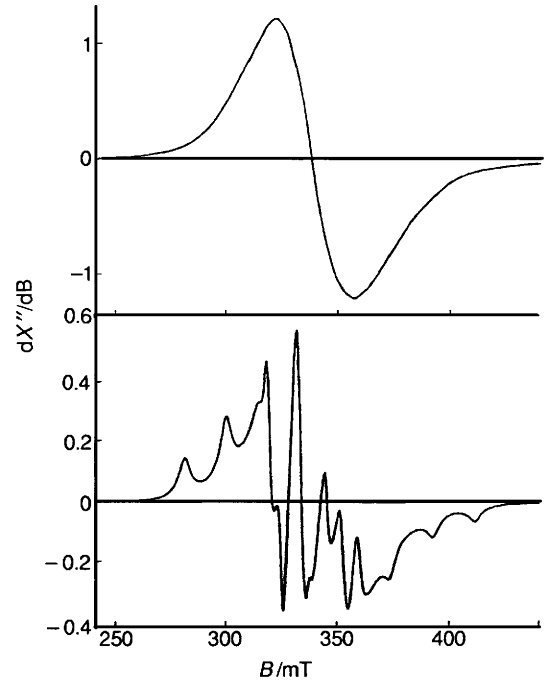


Fig. 1 X-Band ESR spectrum of [L′O(H_2O)V(μ-O)WO_2L]Cl(ClO_4) at 10 K. Top: solid-state spectrum. Bottom: frozen methanol solution spectrum (microwave frequency: 9.4295 GHz; 20 μW per 40 dB)

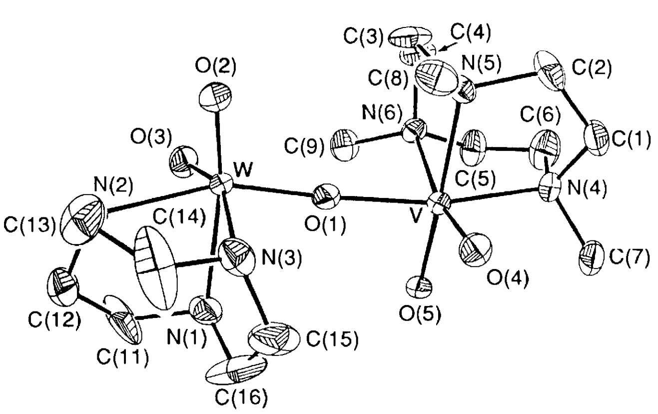


Fig. 2 Structure of the heterodinuclear dication in crystals of complex **1**

The electronic spectrum of complex **3** in MeCN displays absorption maxima at 1150 ($\varepsilon \approx 60$), 760 (112), 491 (1.3×10^3) and 332 nm (3.1×10^3 dm^3 mol^{-1} cm^{-1}). From magnetic susceptibility measurements on a powdered sample in the temperature range 81–293 K a temperature-dependent magnetic moment of 2.4 μ_B at 293 K and 1.9 μ_B at 81 K has been calculated. Complex **3** is a mixed-valence $Mo^{III}Mo^{IV}$ species with most probably delocalized valencies.[8]

Crystal Structures.—Crystals of complex **1** consist of discrete dinuclear heterobimetallic cations [L′O(H_2O)V(μ-O)WO_2L]$^{2+}$, chloride and perchlorate anions. Table 1 summarizes important bond distances and angles; Fig. 2 shows the structure of the dication. Both the vanadium and tungsten centres are in a distorted-octahedral ligand environment. They are connected by an asymmetric oxo bridge. The V–O_b distance is at 1.938(6) Å whereas the W–O_b bond length is shorter at 1.797(6) Å. The

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* Yellow [$Mo(O_3SMe)_3L'$] may be prepared from [MoX_3L'] (X = Br or Cl) in $MeSO_3H$.[7]

Table 1 Selected bond distances (Å) and angles (°) for complex **1**

O(1)–W	1.797(6)	O(2)–W	1.755(5)
O(3)–W	1.713(6)	N(1)–W	2.267(6)
N(2)–W	2.245(7)	N(3)–W	2.306(8)
O(1)–V	1.938(6)	O(4)–V	1.587(6)
O(5)–V	2.028(5)	N(4)–V	2.161(7)
N(5)–V	2.153(6)	N(6)–V	2.356(6)
O(1)–V–O(4)	102.7(3)	O(1)–V–O(5)	89.9(2)
O(4)–V–O(5)	100.7(2)	O(1)–V–N(4)	163.3(3)
O(4)–V–N(4)	93.6(3)	O(5)–V–N(4)	90.2(2)
O(1)–V–N(5)	92.5(2)	O(4)–V–N(5)	95.4(1)
O(5)–V–N(5)	162.8(2)	N(4)–V–N(5)	82.6(2)
O(1)–V–N(6)	86.8(2)	O(4)–V–N(6)	168.7(3)
O(5)–V–N(6)	85.2(2)	N(4)–V–N(6)	76.6(2)
N(5)–V–N(6)	78.0(2)	V–O(1)–W	173.4(3)
O(2)–W–O(1)	104.1(3)	O(3)–W–O(1)	104.9(3)
O(3)–W–O(2)	106.5(3)	N(1)–W–O(1)	88.1(2)
N(1)–W–O(2)	155.8(3)	N(1)–W–O(3)	89.9(3)
N(2)–W–O(1)	157.1(2)	N(2)–W–O(2)	88.1(3)
N(2)–W–O(3)	89.6(3)	N(2)–W–N(1)	74.1(2)
N(3)–W–O(1)	88.8(3)	N(3)–W–O(2)	86.7(3)
N(3)–W–O(3)	157.4(3)	N(3)–W–N(1)	72.5(3)
N(3)–W–N(2)	72.3(3)		

Table 2 Selected bond distances (Å) and angles (°) for complex **2**

Mo(1)–N(1)	2.349(5)	Mo(2)–N(4)	2.206(5)
Mo(1)–N(2)	2.340(4)	Mo(2)–N(5)	2.186(4)
Mo(1)–N(3)	2.322(6)	Mo(2)–N(6)	2.208(7)
Mo(1)–O(1)	1.808(4)	Mo(2)–O(1)	2.034(4)
Mo(1)–O(2)	1.699(3)	Mo(2)–O(4)	2.047(4)
Mo(1)–O(3)	1.702(4)	Mo(2)–O(5)	2.038(4)
Mo(1)–O(1)–Mo(2)	164.9(2)	N(4)–Mo(2)–N(5)	80.3(2)
N(1)–Mo(1)–N(2)	73.5(2)	N(4)–Mo(2)–N(6)	80.5(2)
N(1)–Mo(1)–N(3)	73.7(2)	N(5)–Mo(2)–N(6)	80.3(2)
N(2)–Mo(1)–N(3)	74.1(2)	N(4)–Mo(2)–O(1)	94.5(2)
N(1)–Mo(1)–O(1)	88.3(2)	N(5)–Mo(2)–O(1)	93.4(2)
N(2)–Mo(1)–O(1)	90.6(2)	N(6)–Mo(2)–O(1)	172.5(2)
N(3)–Mo(1)–O(1)	159.0(2)	N(4)–Mo(2)–O(4)	97.6(2)
N(1)–Mo(1)–O(2)	88.7(2)	N(5)–Mo(2)–O(4)	175.6(2)
N(2)–Mo(1)–O(2)	155.9(2)	N(6)–Mo(2)–O(4)	95.6(2)
N(3)–Mo(1)–O(2)	85.6(2)	O(1)–Mo(2)–O(4)	90.6(2)
O(1)–Mo(1)–O(2)	105.2(2)	N(4)–Mo(2)–O(5)	171.0(2)
N(1)–Mo(1)–O(3)	155.8(2)	N(5)–Mo(2)–O(5)	93.8(2)
N(2)–Mo(1)–O(3)	86.3(2)	N(6)–Mo(2)–O(5)	91.9(2)
N(3)–Mo(1)–O(3)	88.2(2)	O(1)–Mo(2)–O(5)	92.6(2)
O(1)–Mo(1)–O(3)	105.5(2)	O(4)–Mo(2)–O(5)	87.9(2)
O(2)–Mo(1)–O(3)	106.2(2)		

V–O–W bridge is nearly linear [173.4(3)°]. The vanadium(IV) ion is co-ordinated facially to a tridentate 1,4,7-trimethyl-1,4,7-triazacyclononane; a terminal V=O group is clearly identified by its very short bond distance at 1.587(6) Å which is in agreement with values for many mononuclear octahedral vanadyl complexes;[9] the octahedral co-ordination sphere is completed by a weakly bound water molecule [V–O 2.028(5) Å]. The three V–N bonds are not equivalent. They correspond nicely to the increasing *trans* influence of the three differing V–O bonds. Thus the V–N bond distance in *trans* position to the short V=O$_t$ bond is quite long at 2.356(6) Å whereas the corresponding distance in *trans* position to the V–OH$_2$ group is the shortest at 2.153(6) Å. The geometry around the vanadium ion in **1** is very similar to the one found in the recently characterized mononuclear [VO(acac)L′]$^+$ cation.[10]

The tungsten(VI) ion is co-ordinated to a tridentate 1,4,7-triazacyclononane ligand and two terminal oxo ligands in *cis* position relative to each other; a sixth co-ordination site is occupied by the bridging oxo ligand. The dimensions of the *cis*-dioxo(1,4,7-triazacyclononane)tungsten(VI) moiety are very similar to those in [(WO$_2$L)$_2$(μ-O)][S$_2$O$_6$]·4H$_2$O and [WO$_3$L]·3H$_2$O.[2] An average W–O$_t$ distance at 1.74 Å and an O$_t$–W–O$_t$ bond angle of 106.5(3)° are typical for the W^{VI}O$_2$ unit with W=O double bonds.

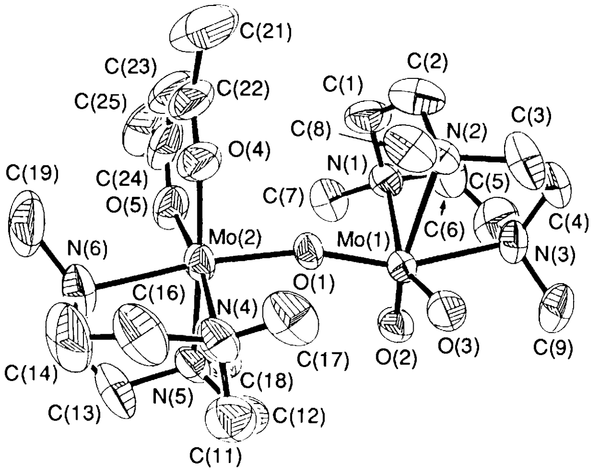

Fig. 3 Structure of the asymmetric dication in crystals of complex **2**

In the solid state the dinuclear cations form two N–H ··· Cl and one O–H ··· Cl contacts with the chloride anion; Cl(1) ··· O(5) at 3.003 Å and Cl(1) ··· N(1) at 3.202 Å represent moderately strong hydrogen-bonding contacts; the contact N(2) ··· Cl(1) at 3.297 Å is very weak. The existence of these hydrogen bonds may explain why the mixed-anion perchlorate salt **1** precipitates and not the diperchlorate salt despite the fact that under our experimental conditions the ClO$_4^-$ concentration exceeds that of the Cl$^-$ anions.

Crystals of complex **2** consist of discrete dinuclear cations [L′(acac)Mo(μ-O)MoO$_2$L′]$^{2+}$ and tetraphenylborate anions. Table 2 gives selected bond distances and angles. Fig. 3 displays the structure of the dication. The asymmetric dication is composed of two octahedral moieties, *i.e.* L′Mo^{III}(acac) and L′MoO$_2$, which are connected by an asymmetric oxo bridging ligand. The metal ion in the *cis*-L′MoO$_2$ fragment is clearly a molybdenum(VI) ion. The dimensions of this entity are very similar to those found in [Mo$^{VI}_2$O$_4$(μ-O)L′$_2$][Br$_3$]$_2$:[11] the Mo=O$_t$ distances in **2** are short at 1.70 Å and the O$_t$–Mo–O$_t$ angle is obtuse (106°) and, characteristically, the two Mo–N bond distances in *trans* position to the Mo=O$_t$ ligands are slightly longer than the one *trans* to the Mo–O$_b$ bond. The Mo–O$_b$ distance in the above symmetrical dinuclear molybdenum(VI) complex is 1.898(1) Å and the Mo–O–Mo angle is 180°. In contrast, in the present mixed-valence dication **2** the Mo^{VI}–O$_b$ distance is *shorter* [1.808(4) Å] and the Mo^{III}–O–Mo^{VI} bridge angle is not linear [164.9(2)°].

The L′Mo^{III}(acac) fragment is bound to the L′Mo^{VI}O$_2$ unit *via* an oxo bridge; the Mo^{III}–O$_b$ distance at 2.034(4) Å is longer than in the symmetrical diamagnetic dinuclear molybdenum(III) complex [Mo$^{III}_2$(MeCN)$_{10}$(μ-O)]$^{4+}$ where this distance is at 1.847(3) Å.[12] These observations suggest that the canonical structure **A** best describes the oxo bridge in this Mo^{III}Mo^{VI}

$$\mathrm{Mo^{III}} \longleftarrow \bar{\mathrm{O}}{=}\mathrm{Mo^{VI}}$$

A

species. The Mo–N bond lengths in the L′Mo^{III}(acac) fragment are significantly shorter than in the L′Mo^{VI}O$_2$ unit. This is somewhat counterintuitive if one considers the larger effective ionic radius of an octahedral Mo^{III} (0.83 Å) as compared to its octahedral Mo^{VI} counterpart (0.73 Å).[13] However, we believe it only reflects the pronounced *trans* influence of the three Mo^{VI}=O bonds in the L′Mo^{VI}O$_3$ part of the dinuclear cation which leads to a significant weakening of the Mo^{VI}–N bonds.

Table 3 Crystallographic data[a] for [L′O(H_2O)V(μ-O)WO_2L]Cl(ClO_4) **1** and [L′(acac)Mo(μ-O)MoO_2L′][BPh_4]$_2$ **2**

Complex	**1**	**2**
Colour	Blue	Brown
Formula	$C_{15}H_{38}Cl_2N_6O_9VW$	$C_{71}H_{89}B_2Mo_2N_6O_5$
M	752.2	1320.0
Crystal dimensions/mm	0.40 × 0.46 × 0.51	0.40 × 0.50 × 0.50
Space group	$P2_1/c$	$P2_1/a$
a/Å	9.401(8)	18.589(9)
b/Å	20.61(1)	18.30(1)
c/Å	13.53(1)	20.432(9)
β/°	102.47(7)	104.73(4)
U/Å^3	2559.76	6722.10
D_c/g cm^{-3}	1.95	1.30
μ(Mo-Kα)/mm^{-1}	5.21	4.1
Transmission coefficients	0.673–0.847	0.92–1.0
Total data collected	6436	16 700
Independent data [$I \geqslant 2.5\sigma(I)$]	5047	8195
Total variables	308	439
R^b	0.051	0.060
R'^b	0.049	0.054
Residual electron density/e Å^{-3}	1.86 (−1.27)	0.97 (−0.53)

[a] Details in common: Syntex R3 diffractometer; Mo-Kα radiation (λ = 0.710 73 Å); monoclinic; $Z = 4$; $3 \leqslant 2\theta \leqslant 55°$; ω scans. [b] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$ with weights $w = \sigma_F$.

Table 4 Atom coordinates (× 10^4) for complex **1**

Atom	x	y	z
W	722(1)	2228(1)	3433(1)
N(1)	2125(8)	2147(3)	5017(5)
N(2)	2255(7)	1399(3)	3384(5)
N(3)	−102(8)	1349(4)	4203(6)
C(11)	3562(11)	1927(6)	4908(9)
C(12)	3580(10)	1416(6)	4218(8)
C(13)	1482(14)	773(5)	3317(8)
C(14)	542(13)	735(5)	4027(13)
C(15)	156(12)	1486(8)	5308(8)
C(16)	1519(17)	1757(6)	5728(7)
O(1)	−495(6)	2736(3)	3946(4)
O(2)	−352(7)	1937(3)	2294(4)
O(3)	1964(7)	2750(3)	3109(5)
V	−1987(1)	3230(1)	4400(1)
O(4)	−2753(6)	2698(3)	4956(4)
O(5)	−466(5)	3577(3)	5579(3)
N(4)	−3472(7)	3991(3)	4619(5)
N(5)	−3486(7)	3139(3)	2960(5)
N(6)	−1312(7)	4111(3)	3490(4)
C(1)	−4920(9)	3737(5)	4026(7)
C(2)	−4869(9)	3497(5)	3005(7)
C(3)	−2774(11)	3410(5)	2173(6)
C(4)	−2160(10)	4066(5)	2435(6)
C(5)	−1751(10)	4686(4)	3997(8)
C(6)	−3186(11)	4625(5)	4213(8)
C(7)	−3561(9)	4030(5)	5692(6)
C(8)	−3786(10)	2444(5)	2693(7)
C(9)	262(9)	4146(4)	3506(7)
Cl(1)	−2804(2)	6459(1)	3940(1)
Cl(2)	6540(3)	249(1)	3513(2)
O(11)	7088(13)	263(7)	4536(8)
O(12)	7318(11)	−203(5)	3103(11)
O(13)	5087(9)	133(6)	3260(10)
O(14)	6809(12)	862(5)	3173(8)

The six-membered Mo(acac) ring is within experimental error planar and the O–C and C–C distances are as those in many structurally characterized M(acac) complexes.

In summary, the crystal structure of complex **2** fully supports the view of localized valencies in the asymmetric dinuclear cation.

Experimental

The macrocycles 1,4,7-triazacyclononane and 1,4,7-trimethyl-1,4,7-triazacyclononane were prepared as described previously.[14]

Preparation of Complexes.—[L′O(H_2O)V(μ-O)WO_2L]Cl(ClO_4) **1**. The complex [VCl_3L′][10] (0.30 g) was dissolved in methanol–water (4:1, 20 cm^3) in the presence of air with gentle heating. To the clear violet solution [WO_3L]·3H_2O[2] (0.32 g) was added. After heating to reflux for 1 h $NaClO_4$·H_2O (0.40 g) was added which initiated the precipitation of bluish green microcrystals which were collected by filtration and recrystallized from the minimum amount of water. Blue crystals suitable for single-crystal X-ray crystallography were obtained from such a solution within 2–3 d (yield: 0.21 g, 31%) (Found: C, 24.1; H, 5.1; N, 10.9. Calc. for $C_{15}H_{38}Cl_2N_6O_9VW$: C, 24.0; H, 5.1; N, 11.2%).

[L′(acac)Mo^{III}(μ-O)MoO_2L′]X_2 **2** (X = PF_6 *or* BPh_4). To a suspension of [$MoBr_3$L′] (or [$MoCl_3$L′])[15] (2.0 g) in water (50 cm^3) was added sodium pentane-2,4-dionate (3.0 g). The mixture was heated to reflux for 2 h in the presence of air. Upon addition of KPF_6 (2.5 g) to the clear brown solution brown crystals precipitated which were collected by filtration, washed with ethanol and diethyl ether and air-dried (yield: 63% based on [MoX_3L]). Crystals of the tetraphenylborate salt of **2** suitable for an X-ray structure determination were obtained from a methanol–MeCN (1:1) solution of the PF_6 salt by addition of Na[BPh_4] (Found: C, 25.0; H, 3.8; N, 7.5. Calc. for $C_{23}H_{49}F_{12}Mo_2N_6O_5P_2$: C, 24.7; H, 3.4; N, 7.5%).

[$Mo_2L'_2$(acac)$_2$(μ-O)][PF_6]$_3$ **3**. To an argon-purged solution of sodium pentane-2,4-dionate (2.0 g) in water (50 cm^3) was added [Mo(O_3SMe)$_3$L′][7] (1.0 g). The mixture was stirred under an argon atmosphere at 20 °C for 30 min until a clear brown solution was obtained. After addition of KPF_6 (2.0 g) the stirring was continued in the presence of air. A violet microcrystalline solid formed which was collected by filtration, washed with water and ether and air-dried (yield: 30%) (Found: C, 28.8; H, 4.8; N, 7.3. Calc. for $C_{28}H_{56}F_{18}Mo_2N_6O_5P_3$: C, 28.4; H, 4.7; N, 7.1%).

X-Ray Crystallography.—Crystal data and details of the intensity collection for complexes **1** and **2** are summarized in Table 3. Atom coordinates are given in Tables 4 and 5 for complexes **1** and **2**, respectively. Graphite-monochromated Mo-Kα radiation was used throughout. Crystal stabilities were monitored by recording three check reflections after every 400 measurements; no deterioration was observed. The two data sets were corrected for Lorentz and polarization effects, also for absorption (ψ scans of seven reflections, respectively). The structures were solved by conventional Patterson and Fourier-difference syntheses. Both structures were refined[16] by full-matrix least-squares techniques; the function minimized was $\Sigma w(|F_o| - |F_c|)^2$ where $w = 1/\sigma^2(|F_o|)$. Neutral atom scattering factors were taken from ref. 17 and hydrogen-atom scattering factors from ref. 18. The positions of the methyl and methylene protons were calculated and included in the final refinement cycles with isotropic thermal parameters. For complex **1** all non-hydrogen atoms were refined with anisotropic thermal parameters. For **2** the carbon atoms of the phenyl rings of the BPh_4^- anion were refined as rigid bodies with isotropic thermal parameters only. The maximum residual electron density (1.8 e Å^{-3}) in the final Fourier difference map of **1** is located in the

Table 5 Atomic coordinates (× 10^4) for complex **2**

Atom	*x*	*y*	*c*	Atom	*x*	*y*	*z*
Mo(1)	3760(1)	942(1)	2381(1)	C(36)	193(2)	6929(2)	4476(2)
Mo(2)	2068(1)	445(1)	3019(1)	C(37)	836	7200	4331
N(1)	3906(3)	−239(3)	1981(2)	C(38)	1301	6732	4087
N(2)	3166(3)	941(3)	1224(2)	C(39)	1121	5993	3988
N(3)	4701(3)	1020(3)	1823(3)	C(40)	477	5722	4133
N(4)	1891(3)	1612(3)	3199(3)	C(41)	13	6190	4377
N(5)	2782(3)	555(3)	4044(2)	C(42)	168(2)	8076(2)	5316(2)
N(6)	1224(3)	344(3)	3603(3)	C(43)	287	8801	5159
O(1)	2916(2)	631(2)	2578(2)	C(44)	753	9246	5640
O(2)	4452(2)	754(2)	3082(2)	C(45)	1101	8967	6277
O(3)	3690(3)	1869(2)	2336(2)	C(46)	982	8242	6434
O(4)	1332(2)	365(3)	2087(2)	C(47)	516	7797	5954
O(5)	2197(2)	−659(2)	2996(2)	C(48)	−1015(2)	7048(2)	5046(2)
C(1)	3227(4)	−380(4)	1418(3)	C(49)	−1776	7134	4762
C(2)	3057(4)	207(4)	922(3)	C(50)	−2286	6757	5032
C(3)	3647(5)	1393(4)	901(4)	C(51)	−2035	6294	5586
C(4)	4415(5)	1203(5)	1096(3)	C(52)	−1274	6209	5870
C(5)	5093(4)	298(5)	1927(4)	C(53)	−764	6586	5600
C(6)	4581(4)	−311(4)	1731(4)	B(2)	−366(4)	7379(4)	303(3)
C(7)	3928(4)	−770(3)	2533(3)	C(54)	184(2)	7051(2)	1028(2)
C(8)	2444(4)	1306(4)	1124(3)	C(55)	754	6566	999
C(9)	5232(4)	1599(4)	2163(4)	C(56)	1226	6300	1595
C(11)	2444(4)	1851(4)	3838(3)	C(57)	1126	6518	2221
C(12)	3048(4)	1323(4)	4089(3)	C(58)	556	7002	2250
C(13)	2352(4)	389(5)	4553(3)	C(59)	85	7269	1654
C(14)	1649(5)	22(5)	4255(4)	C(60)	−978(2)	7975(2)	486(2)
C(15)	932(5)	1082(5)	3710(5)	C(61)	−860	8728	479
C(16)	1110(4)	1641(4)	3271(4)	C(62)	−1355	9206	669
C(17)	1948(4)	2096(3)	2625(3)	C(63)	−1967	8932	867
C(18)	3450(3)	71(4)	4165(3)	C(64)	−2085	8179	874
C(19)	594(4)	−151(5)	3279(4)	C(65)	−1590	7701	684
C(21)	712(5)	−78(5)	1016(4)	C(66)	184(2)	7822(2)	−129(2)
C(22)	1196(4)	−202(5)	1712(4)	C(67)	−128	8049	−792
C(23)	1456(5)	−907(5)	1899(5)	C(68)	307	8415	−1151
C(24)	1932(5)	−1101(4)	2510(5)	C(69)	1055	8555	−847
C(25)	2180(5)	−1877(4)	2635(5)	C(70)	1368	8328	−184
B(1)	−389(4)	7524(4)	4724(3)	C(71)	932	7962	175
C(30)	−837(2)	8014(2)	4053(2)	C(72)	−868(2)	6720(2)	−187(2)
C(31)	−769	7853	3404	C(73)	−695	5979	−101
C(32)	−1164	8260	2852	C(74)	−1129	5464	−529
C(33)	−1627	8828	2948	C(75)	−1736	5690	−1044
C(34)	−1695	8989	3597	C(76)	−1908	6432	−1130
C(35)	−1301	8582	4149	C(77)	−1474	6947	−702

proximity of the tungsten atom at a chemically unreasonable distance.

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