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The redox chemistry of $LMO_3 \cdot 3H_2O$ (M = Mo(VI), W(VI); L = 1,4,7-triazacyclononane). The crystal structures of *anti*-$[L_2W_2Cl_2(\mu\text{-}O)(\mu\text{-}OH)]ZnCl_4 \cdot 2H_2O$ and $[L_3Mo_3O_4][Zn(Cl,Br)_4]_2 \cdot H_2O$

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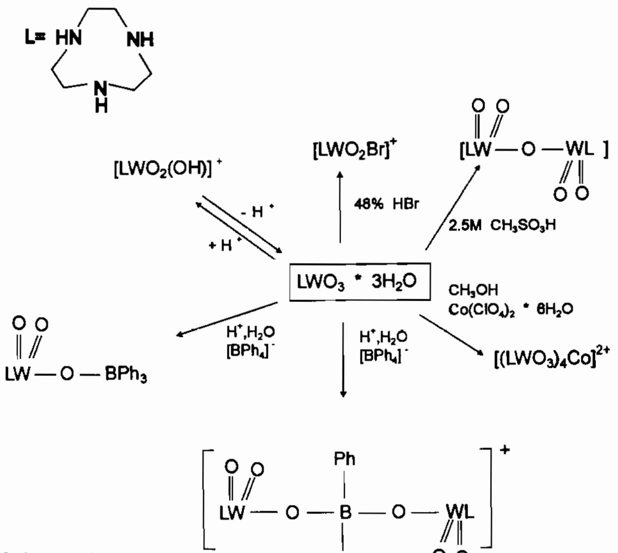
Abstract

Reduction of $LWO_3 \cdot 3H_2O$ (L = 1,4,7-triazacyclononane; $C_6H_{15}N_3$) with zinc powder in 2.5 M aqueous CH_3SO_3H solutions under anaerobic conditions affords green solutions from which upon addition of NaX (X = Br, I) green microcrystals were obtained: X = Br: *anti*-$[L_2W_2^{III}Br_2(\mu\text{-}OH)_2]Br_2 \cdot 2H_2O$ (**1**); X = I: $[L_2W_2^{III}I_2(\mu\text{-}OH)_2]I_2 \cdot 2H_2O$, (**2**). In contrast, when X = Cl the paramagnetic mixed valent complex *anti*-$[L_2W_2Cl_2(\mu\text{-}O)(\mu\text{-}OH)]ZnCl_4 \cdot 2H_2O$ (**3**) has been isolated and its crystal structure has been determined. Crystal data of **3**: orthorhombic space group $P2_12_12_1$; $a = 9.603(4)$, $b = 10.444(4)$, $c = 27.20(1)$ Å; $Z = 4$. The short W–W distance of 2.431(1) Å indicates a strong metal–metal bond. Complex **3** is reduced in 2.0 M HCl by zinc yielding diamagnetic *anti*-$[L_2W_2^{III}Cl_2(\mu\text{-}OH)_2]ZnCl_4 \cdot 2H_2O$ (**4**). The trinuclear complex $[L_3Mo_3O_4][ZnCl_4]_2 \cdot 2H_2O$ (**6**) has also been prepared and its crystal structure has been determined. Crystal data for $[L_3Mo_3O_4][Zn(Cl,Br)_4]_2 \cdot 2H_2O$: orthorhombic space group *Pnmb*; $a = 13.820(4)$, $b = 14.740(5)$, $c = 19.810(7)$ Å; $Z = 4$.

Introduction

Recently we have reported the synthesis and crystal structure of monomeric, octahedral *cis*-trioxo(1,4,7-triazacyclononane)tungsten(VI)trihydrate, $LWO_3 \cdot 3H_2O$ [1, 2]. A unique feature of this species is its excellent solubility in water and its kinetic stability toward ligand dissociation over a wide range of pH (0–8) contrasting in this respect its open chain analogue (dien)WO_3 (dien = diethylenetriamine) [3]. It has therefore been possible to investigate the basicity and nucleophilicity of the *cis*-trioxotungsten(VI) fragment in solution. Protonation, dimerization and the replacement of oxo ligands by halides in acidic aqueous media have been observed [1] and, in addition, we have discovered that LWO_3 can function as a ligand in weakly coordinating solvents when an oxophilic main group or transition element acts as an acceptor [4]. Scheme 1 summarizes some pertinent reactions.



Scheme 1.

Here we report the redox chemistry of $LWO_3 \cdot 3H_2O$ and its molybdenum(VI) analogue in acidic aqueous solution. Formation of strongly metal–metal bonded dimers such as *anti*-$[L_2W_2^{III}Cl_2(\mu\text{-}OH)_2]ZnCl_4 \cdot 2H_2O$ and its mixed valent $W^{III}W^{IV}$ form *anti*-$[L_2W_2Cl_2(\mu\text{-}$

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OH)(μ-O)]$ZnCl_4 \cdot 2H_2O$, and the very reactive complex *anti*-[$L_2W_2^{III}I_2(\mu\text{-OH})_2$]$I_2 \cdot 2H_2O$ are described. In addition, [$L_3M_3O_4$][$ZnCl_4$]$_2$ (M = Mo, W) [5] complexes have been prepared and the crystal structure of the molybdenum complex has been determined.

Experimental

$LWO_3 \cdot 3H_2O$ was prepared as described previously [1]. All reactions were carried out under rigorous anaerobic conditions under an argon blanketing atmosphere.

Syntheses of complexes

anti-[L$_2$W$_2$Br$_2$(μ-OH)$_2$]Br$_2$·2H$_2$O (1)

To a solution of $LWO_3 \cdot 3H_2O$ (0.40 g; 1 mmol) in 2.5 M aqueous CH_3SO_3H (30 ml) was added zinc powder (1.0 g) whereupon a dark green solution was obtained. After stirring of this solution at room temperature for 45 min the zinc powder was removed by filtration and solid NaBr (1.5 g) was added to the clear solution. After standing at 2 °C for 12 h green crystals precipitated out (yield 0.20 g, 49%). **1** has previously been prepared by using [$LWOBr_2$]Br as starting material [5]. *Anal.* Calc. for $C_{12}H_{36}N_6O_4Br_4W_2$: C, 14.2; H, 3.6; N, 8.3. Found: C, 14.4; H, 3.5; N, 8.5%.

anti-[L$_2$W$_2$I$_2$(μ-OH)$_2$]I$_2$·2H$_2$O (2)

This compound was prepared as described above for **1** using NaI instead of NaBr. Green, very air sensitive microcrystals were obtained (yield 0.22 g; 43%). *Anal.* Calc. for $C_{12}H_{36}N_6O_4I_4W_2$: C, 12.0; H, 3.0; N, 7.0. Found: C, 11.8; H, 2.8; N, 6.8%.

anti-[L$_2$W$_2$Cl$_2$(μ-O)(μ-OH)]ZnCl$_4$·2H$_2$O (3)

To a solution of $LWO_3 \cdot 3H_2O$ (0.30 g; 0.7 mmol) in 2.5 M aqueous CH_3SO_3H (25 ml) was added zinc powder (1.0 g). The resulting green solution was stirred at room temperature for 1 h after which time the undissolved zinc was removed by filtration, and solid NaCl (1.2 g) was added. Further addition of NaCl (1.2 g) after 12 h and standing at 2 °C in the refrigerator for 3 days initiated the precipitation of dark green crystals which were collected by filtration (yield 0.16 g; 45%). *Anal.* Calc.. for $C_{12}H_{35}Cl_6N_6O_4W_2Zn$: C, 14.8; H, 3.6; N, 8.6. Found: C, 14.4; H, 3.7; N, 8.2%.

anti-[L$_2$W$_2$Cl$_2$(μ-OH)$_2$]ZnCl$_4$·2H$_2$O (4)

A solution of *anti*-[$L_2W_2Br_2(\mu\text{-OH})_2$]$Br_2 \cdot 2H_2O$ (**1**) [5] (0.13 g; 0.13 mmol) in 2.0 M hydrochloric acid (40 ml) to which zinc amalgam (3 ml) had been added, was stirred at ambient temperature for 3 h. Addition of $ZnCl_2$ (2.0 g) initiated the precipitation of green microcrystals (yield 0.080 g, 68%). *Anal.* Calc. for $C_{12}H_{36}N_6O_4Cl_6W_2Zn$: C, 14.8; H, 3.7; N, 8.6; Cl, 21.8. Found: C, 14.6; H, 3.3; N, 8.4; Cl, 21.6%.

[L$_3$W$_3$O$_4$](ZnBr$_4$)$_2$ (5)

To a solution of $LWO_3 \cdot 3H_2O$ (0.20 g; 0.5 mmol) in 2.5 M aqueous CH_3SO_3H was added zinc powder (0.7 g). The green solution was stirred at room temperature for 1 h after which time the residual zinc was removed by filtration. Addition of $LWO_3 \cdot 3H_2O$ (0.19 g; 0.25 mmol) and NaBr (2.0 g) to this solution initiated the precipitation of brown microcrystals (yield 0.28 g; 65%). This complex had been obtained previously by using a different route [5].

[L$_3$Mo$_3$O$_4$](ZnCl$_4$)$_2$·2H$_2$O (6)

A solution of $LMoO_3 \cdot 3H_2O$ [2] (0.50 g; 1.5 mmol) in 0.5 M aqueous CH_3SO_3H (25 ml) was reduced at room temperature by addition of zinc powder (1.0 g) and stirring for 1 h to give a clear green solution. After removal of residual zinc by filtration $LMoO_3 \cdot 3H_2O$ (0.25 g; 0.75 mmol) was added. The color of the solution changed immediately to red which faded back to greenish within minutes. The solution was kept for 4 weeks at room temperature under an argon atmosphere whereupon the color changed slowly to red again. In the presence of air the solution was then passed through a Dowex 50-X-2 column (diam. 1 cm; length 20 cm). Elution with 1.0 M and then with 4.0 M hydrochloric acid produced a yellow and a red–purple fraction, respectively. Addition of $ZnCl_2$ (2.0 g) to the latter initiated the precipitation of red microcrystals of **6** (yield 0.03 g; 5%). *Anal.* Calc. for $C_{18}H_{49}N_9Mo_3O_6Cl_8Zn_2$: C, 18.2; H, 4.2; N, 10.6. Found: C, 18.2; H, 4.1; N, 10.6%.

Crystals of **6** suitable for X-ray crystallography were obtained from an 0.5 M HCl solution of **6** to which a small amount of KBr was added. The red crystals obtained contained partially bromide substituted $ZnCl_4^-$ counteranions.

X-ray crystallography

Intensities and lattice parameters of a blue–green tabular shaped crystal of **3** and of a dark red tabular shaped crystal of **6** were measured at room temperature on a Syntex R3 and an AED II (Siemens) diffractometer, respectively. Crystal parameters and additional details of the data collection and refinement are given in Table 1. Empirical absorption corrections (Ψ scans) were carried out in both cases (7 reflections in the range $4 < 2\theta < 23°$). Both structures were solved by conventional Patterson and difference Fourier methods and refined with anisotropic thermal parameters for all non-hydrogen atoms. Neutral-atom scattering factors and

TABLE 1. Crystallographic data for *anti*-$[L_2W_2Cl_2(\mu\text{-}O)(\mu\text{-}OH)]ZnCl_4 \cdot 2H_2O$ (**3**) and $[L_3Mo_3O_4][Zn(Cl,Br)_4] \cdot H_2O$ (**6**)

	3	**6**
Chemical formula	$C_{12}H_{35}N_6O_4Cl_6W_2Zn$	$C_{18}H_{47}N_9Mo_3O_5(Cl,Br)_8Zn_2$
Formula weight	973.2	
Space group	$P2_12_12_1$ (No. 19)	*Pnmb* (No. 62)
a (Å)	9.603(4)	13.820(4)
b (Å)	10.444(4)	14.740(5)
c (Å)	27.20(1)	19.810(7)
V (Å^3)	2728(1)	4035.4(20)
Z	4	4
T (°C)	22	22
λ (Å)	0.71069	0.71069
ρ_{calc} (g cm^{-3})	2.36	~1.95
μ(Mo Kα) (cm^{-1})	101.2	26.7
Transmission coefficient (%)	60–98	65–98
$R(F_o)$[a]	0.037	0.051
$R(F_o^2)$[b]	0.032	0.043
GOF[c]	1.94	2.25

[a] $R(F_o) = \Sigma|\Delta F|/\Sigma|F_o|$. [b] $R_w(F_o^2) = [\Sigma w\Delta F^2/\Sigma|F_o|^2]^{1/2}$; $w = 1/\sigma^2(F)$. [c] $[\Sigma w\Delta F^2/(N_o - N_v)]^{1/2}$; N_o = number of observations, N_v = number of variables.

anomalous dispersion corrections for non-hydrogen atoms were taken from ref. 6. All methylene and amine hydrogen atoms were placed at calculated positions with isotropic temperature factors. The hydrogen atoms of the OH bridge and of water molecules of crystallization were not located. The function minimized during full-matrix least-squares refinement was $\Sigma w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F)$. Since **3** crystallizes in the acentric space group $P2_12_12_1$ the absolute configuration of the enantiomeric dication in the crystal of **3** was checked. Crystals of **6** suitable for X-ray crystallography were grown from a solution of the tetrachlorozincate salt to which KBr had been added to improve crystallization and, consequently, the crystal used contained a small amount of coordinated bromide ions. By treating the occupancy factors of the chloride positions as variables it was found that only the Cl(1) and Cl(4) positions were partially occupied by bromide ions (ratios Cl(1)/Br ≈ 3/2 and Cl(4)/Br ≈ 4/1). Final atom coordinates are given in Table 2 for **3** and Table 3 for **6**.

Results and discussion

Synthesis

Scheme 2 summarizes the synthetic results. $LWO_3 \cdot 3H_2O$ dissolves readily in 2.5 M CH_3SO_3H at ambient temperature affording a colorless solution. No ligand dissociation was observed. Under strictly anaerobic conditions using an argon blanketing atmosphere zinc powder is a very efficient reducing agent which produces a deep green solution. Addition of solid NaBr to such a solution leads to the precipitation of green, diamagnetic crystals of $[L_2W_2Br_2(\mu\text{-}OH)_2]Br_2 \cdot 2H_2O$ (**1**), the crystal structure of which has been reported [5]. The yields never exceeded 50% based on the starting material $LWO_3 \cdot 3H_2O$.

When NaI is used instead of NaBr in the above preparation diamagnetic green microcrystals precipitated; the yields again did not exceed 50%. Elemental analysis and the IR spectrum are in agreement with the formulation as either $[L_2W_2I_2(\mu\text{-}OH)_2]I_2 \cdot 2H_2O$ or $[L_2W_2(OH_2)_2(\mu\text{-}OH)_2]I_4$. The material is very air sensitive both in solution and in the solid state. From UV–Vis spectral measurements of this species in acidic solution in the presence and absence of excess iodide it is concluded that $[L_2W_2I_2(\mu\text{-}OH)_2]I_2 \cdot 2H_2O$ (**2**) is probably the correct formulation.

Interestingly, when NaCl is added to the above green solution dark green crystals precipitated in 45% yield within 3 days at 2 °C. Elemental analysis and an X-ray crystal structure showed unambiguously that this material is *anti*-$[L_2W_2Cl_2(\mu\text{-}O)(\mu\text{-}OH)]ZnCl_4 \cdot 2H_2O$ (**3**). This complex is paramagnetic. From temperature-dependent susceptibility measurements in the range 98 to 298 K on a powdered sample of **3** using the Faraday method a temperature-independent magnetic moment of 1.75 μ_B per dinuclear unit was calculated which indicates one unpaired electron per W_2 unit. Thus a mixed valence W^{III}/W^{IV} species had formed. We were very careful to ensure the absence of oxygen during the preparation and we are confident that **3** is not produced via oxidation of a W_2^{III} dimer by adventitious oxygen. This preparative result indicates that the reduction of $LWO_3 \cdot 3H_2O$ in acidic aqueous solution by zinc does not produce W^{III} species as the sole product. Instead, the green solution obviously contains $W^{III}W^{IV}$ species of unknown composition and structure.

TABLE 2. Atom coordinates ($\times 10^4$) and temperature factors ($Å^2 \times 10^3$) for *anti*-$[L_2W_2Cl_2(\mu\text{-}O)(\mu\text{-}OH)]ZnCl_4 \cdot 2H_2O$

Atom	*x*	*y*	*z*	*U*[a]
W(1)	6816(1)	4388(1)	8367(1)	21(1)
W(2)	4675(1)	4575(1)	8839(1)	21(1)
Cl(1)	8453(3)	4735(3)	9007(1)	44(1)
Cl(2)	3035(3)	4417(4)	8191(1)	41(1)
O(1)	5703(7)	6102(6)	8478(3)	25(2)
O(2)	5764(7)	3046(7)	8690(3)	31(2)
N(1)	5920(9)	4109(9)	7631(3)	31(3)
N(2)	8106(10)	2842(8)	8060(3)	31(3)
N(3)	8233(9)	5457(8)	7854(3)	33(3)
C(1)	6451(14)	2949(11)	7364(4)	43(4)
C(2)	7180(15)	2069(12)	7731(4)	51(5)
C(3)	9385(11)	3318(11)	7807(4)	40(4)
C(4)	9596(12)	4776(11)	7854(5)	47(4)
C(5)	7677(12)	5644(12)	7355(4)	42(4)
C(6)	6151(13)	5309(13)	7345(4)	43(4)
N(4)	3413(9)	3320(9)	9337(3)	32(3)
N(5)	3197(10)	5974(8)	9177(3)	28(3)
N(6)	5591(9)	4970(8)	9553(3)	30(3)
C(7)	1963(13)	3883(11)	9349(4)	39(4)
C(8)	2061(10)	5312(11)	9472(4)	34(4)
C(9)	4050(13)	6857(11)	9510(4)	39(4)
C(10)	4938(12)	6044(10)	9843(4)	33(3)
C(11)	5557(12)	3747(11)	9835(4)	37(4)
C(12)	4096(13)	3205(11)	9834(4)	39(4)
Zn(1)	8858(1)	8824(1)	8693(1)	32(1)
Cl(11)	7625(4)	8600(3)	8002(1)	45(1)
Cl(12)	7436(3)	8010(3)	9287(1)	44(1)
Cl(13)	9317(4)	10899(3)	8882(1)	58(1)
Cl(14)	10945(4)	7836(4)	8621(1)	69(1)
Wa(1)[b]	5559(14)	588(11)	9131(7)	164(9)
Wa(2)	2755(13)	605(14)	9148(8)	188(10)

[a] Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor. [b] Wa = oxygen atom of water molecule of crystallization.

It is possible to generate the reduced diamagnetic green *anti*-$[L_2W_2Cl_2(\mu\text{-}OH)_2]ZnCl_4 \cdot 2H_2O$ (**4**) either via reduction of **3** in conc. HCl with zinc or via substitution of bromide ions in **1** by chloride (dissolution of **1** in conc. HCl and addition of $ZnCl_2$ under strictly anaerobic conditions). The IR spectra of **3** and **4** are very similar but a significant difference was found in the 700–800 cm^{-1} region. **3** exhibits a band at 761 cm^{-1} which is assigned to the antisymmetric (W–O–W) stretching mode which is not detectable in the spectrum of the reduced complex **4**.

When aqueous green solutions of **1**, **2**, **3** or **4** are exposed to air a rapid color change to purple is observed. Addition of NaI to such a solution initiates the precipitation of *anti*-$[L_2W_2O_2(\mu\text{-}O)_2]I_2$ in $\approx$90% yields. The crystal structure of this W^V_2 dimer has been reported previously [7]. It has been shown that *anti*-$[L_2W_2O_4]^{2+}$ isomerizes (acid catalyzed) to give yellow *cis*-$[L_2W_2O_4]^{2+}$, the crystal structure of which has also been reported [7].

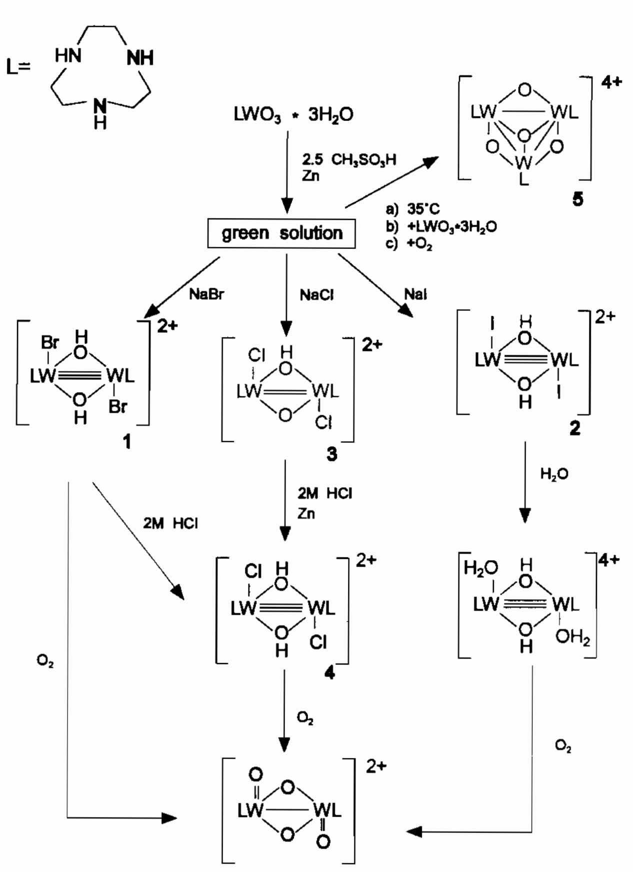
TABLE 3. Atom coordinates ($\times 10^4$) and temperature factors ($Å^2 \times 10^3$) for $[L_3Mo_3O_4][Zn(Cl,Br)_4]_2 \cdot H_2O$ (**6**)

Atom	*x*	*y*	*z*	*U*[a]
Mo(1)	1590(1)	6202(1)	6154(1)	24(1)
Mo(2)	2500	7011(1)	5237(1)	28(1)
O(1)	2500	7322(7)	6247(5)	32(4)
O(2)	1432(5)	6165(5)	5182(3)	30(3)
O(3)	2500	5230(7)	6259(5)	29(4)
N(1)	1250(7)	6154(6)	7264(4)	32(3)
N(2)	208(7)	6990(6)	6263(4)	38(4)
N(3)	497(7)	5117(6)	6202(5)	35(3)
N(4)	2500	7053(10)	4138(6)	43(6)
N(5)	3491(8)	8190(6)	5025(4)	45(4)
C(1)	426(9)	6774(8)	7483(6)	45(5)
C(2)	215(10)	7456(8)	6935(5)	44(5)
C(3)	−692(8)	6383(8)	6203(6)	49(5)
C(4)	−385(9)	5483(8)	5866(5)	47(5)
C(5)	290(10)	4792(8)	6906(5)	44(5)
C(6)	1038(9)	5156(8)	7406(6)	45(5)
C(7)	3382(14)	7479(11)	3886(7)	134(10)
C(8)	3855(11)	8091(10)	4318(6)	65(6)
C(9)	2979(10)	9078(8)	5142(8)	115(9)
Zn(1)	7500	2341(2)	1132(1)	41(1)
Zn(2)	2500	5747(2)	2131(1)	39(1)
Cl(1)	7500	3942(2)	1170(2)	65(2)
Cl(2)	7500	1914(3)	2227(2)	39(2)
Cl(3)	6140(3)	1872(2)	593(2)	52(1)
Cl(4)	2500	7307(3)	2091(2)	47(1)
Cl(5)	2500	5230(3)	3219(2)	36(2)
Cl(6)	3849(3)	5186(2)	1605(1)	42(1)
Wa(1)[b]	4530(7)	6469(6)	447(4)	72(4)

[a] Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor. [b] Wa = oxygen atom of the water molecule of crystallization.

In contrast, when an acidic (2.5 M CH_3SO_3H) Zn reduced solution of $LWO_3 \cdot 3H_2O$ is exposed to air, a brown solution is obtained from which brown crystals of $[L_3W_3O_4]I_4$ crystallize in $\approx$50% yield upon addition of NaI. Ion exchange chromatography showed that such an oxidized solution also contains small amounts of yellow *syn*-$[L_2W_2O_4]^{2+}$. Interestingly, the same trinuclear species forms in low yields (<30%) without addition of an external oxidant such as O_2 upon gentle warming ($\approx$40 °C, 30 min) of the reduced green solution. These experiments clearly indicate that the reduction of $LWO_3 \cdot 3H_2O$ in acidic solution by Zn does not quantitatively produce the dinuclear W^{III} species as the sole product but W^{IV} is also present. The yields of $[L_3W_3O_4]^{4+}$ can be significantly improved ($\approx$65%) via a comproportionation reaction when $LWO_3 \cdot 3H_2O$ is added to the above green reduced solution.

We have also studied the reduction of the corresponding $LMoO_3 \cdot 3H_2O$ species in 2.5 M CH_3SO_3H by Zn. Here also a deep green solution is obtained. Air oxidation of such a solution produces quantitatively *syn*-$[L_2Mo_2O_4]^{2+}$ [8, 9]. Since the electronic spectra of (i) Zn reduced solutions of $LMoO_3 \cdot 3H_2O$, (ii) Zn



Scheme 2.

reduced solutions of *syn*- (or *anti*)-$[L_2Mo_2O_4]^{2+}$, and (iii) a solution of $[L_2Mo_2^{III}(OH_2)_2(\mu\text{-}OH)_2]^{4+}$ [10] are identical, it is concluded that the latter dinuclear species is the sole product in reduced $LMoO_3 \cdot 3H_2O$ solutions.

Since it is well known that trinuclear Mo^{IV} complexes are readily available via comproportionation reactions [11], e.g. eqns. (1) or (2), we attempted to synthesize $[L_3Mo_3O_4]^{4+}$ by adding $LMoO_3 \cdot 3H_2O$ to the above green solution of $[L_2Mo_2(OH_2)_2(\mu\text{-}OH)_2]^{4+}$ in 2.5 M CH_3SO_3H.

$$2Mo^{III} + Mo^{VI} \longrightarrow Mo_3^{IV} \qquad (1)$$

$$Mo_2^{III} + Mo^{VI} \longrightarrow Mo_3^{IV} \qquad (2)$$

At room temperature the color change green to red occurs very slowly within 4 weeks. Warming of the reaction mixture to 60 °C brings about the expected color change within 1 h. Ion exchange chromatography of the resulting solution showed that the red aqua-ion $[(H_2O)_9Mo_3O_4]^{4+}$, yellow *syn*-$[L_2Mo_2O_4]^{2+}$ and protonated, uncoordinated 1,4,7-triazacyclononane had formed. Thus the expected $[L_3Mo_3O_4]^{4+}$ species probably dissociates in this very acidic medium.

When the same reaction is carried out in 0.5 M CH_3SO_3H at room temperature it is possible to isolate the desired complex $[L_3Mo_3O_4]^{4+}$ as the tetrachlorozincate salt after 4 weeks via ion-exchange chromatography in very low yields (≈5%).

Crystal structures

Figure 1 shows the structure of the dication in crystals of **3** and the atom labeling scheme. Table 4 summarizes important bond distances and angles. Crystals of **3** consist of the dinuclear cation *anti*-$[L_2W_2Cl_2(\mu\text{-}O)(\mu\text{-}OH)]^{2+}$, discrete $ZnCl_4^{2-}$ anions and water molecules of crystallization. Compound **3** crystallizes in the acentric space group $P2_12_12_1$; the dication in **3** does not possess crystallographically imposed symmetry. The two tung-

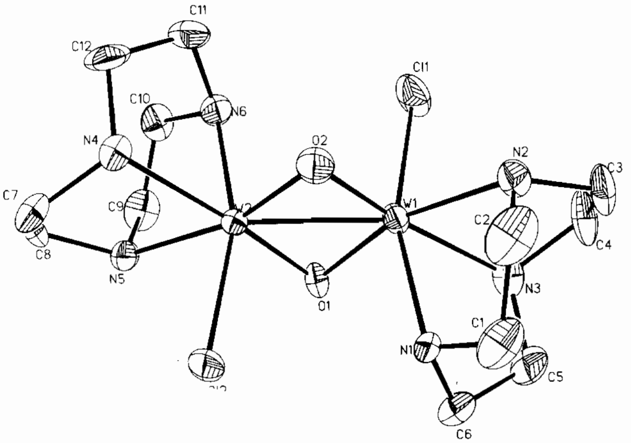


Fig. 1. Structure of the dication in crystals of **3**.

TABLE 4. Selected bond lengths (Å) and angles (°) for *anti*-$[L_2W_2Cl_2(\mu\text{-}O)(\mu\text{-}OH)]ZnCl_4 \cdot 2H_2O$

W(1)–W(2)	2.431(1)	W(1)–Cl(1)	2.373(3)
W(1)–O(1)	2.107(7)	W(1)–O(2)	1.938(7)
W(1)–N(1)	2.198(8)	W(1)–N(2)	2.201(9)
W(1)–N(3)	2.247(9)	W(2)–Cl(2)	2.369(3)
W(2)–O(1)	2.117(7)	W(2)–O(2)	1.951(7)
W(2)–N(4)	2.241(9)	W(2)–N(5)	2.234(9)
W(2)–N(6)	2.171(8)		
Cl(1)–W(1)–O(1)	95.8(2)	O(1)–W(1)–O(2)	106.6(3)
Cl(1)–W(1)–O(2)	97.1(2)	Cl(1)–W(1)–N(1)	161.3(3)
O(1)–W(1)–N(1)	92.5(3)	O(2)–W(1)–N(1)	96.5(3)
O(1)–W(1)–N(2)	164.5(3)	Cl(1)–W(1)–N(2)	91.0(2)
N(1)–W(1)–N(2)	77.1(3)	O(2)–W(1)–N(2)	86.3(3)
Cl(1)–W(1)–N(3)	88.8(2)	O(1)–W(1)–N(3)	88.5(3)
O(2)–W(1)–N(3)	163.1(3)	N(1)–W(1)–N(3)	74.7(3)
N(2)–W(1)–N(3)	77.7(3)	Cl(2)–W(2)–O(1)	91.0(2)
O(1)–W(2)–O(2)	105.7(3)	Cl(2)–W(2)–O(2)	98.3(2)
Cl(2)–W(2)–N(4)	92.8(2)	O(1)–W(2)–N(4)	166.8(3)
O(2)–W(2)–N(4)	86.3(3)	O(1)–W(2)–N(5)	89.7(3)
Cl(2)–W(2)–N(5)	85.9(2)	N(4)–W(2)–N(5)	77.9(3)
O(2)–W(2)–N(5)	163.9(3)	Cl(2)–W(2)–N(6)	161.4(2)
O(1)–W(2)–N(6)	94.8(3)	O(2)–W(2)–N(6)	97.1(3)
N(4)–W(2)–N(6)	77.9(3)	N(5)–W(2)–N(6)	76.4(3)
W(1)–O(1)–W(2)	70.3(2)	W(1)–O(2)–W(2)	77.4(3)

sten ions are bridged by two oxygen atoms (O(1) and O(2)). Interestingly, the average W–O(1) and W–O(2) bond distances are significantly different (2.112 and 1.944 Å) as are the two bond angles W–O(1)–W (70.3(2)°) and W–O(2)–W (77.4(3)°). Thus O(1) is a hydroxo bridge (the proton has not been located in the X-ray structure determination) whereas O(2) is an oxo bridge. The W–$O_{hydroxo}$ bond length in $[L_2W_2Br_2(\mu\text{-}OH)]Br_2 \cdot 2H_2O$ has been determined to be 2.10(2) Å [5] in excellent agreement with values for W–O(1) found here for **3**. The W–W distance at 2.431(1) Å is short and indicates considerable metal–metal bonding. In the di-μ-hydroxo bridged tungsten(III) dinuclear cation $[L_2W_2Br_2(\mu\text{-}OH)_2]^{2+}$ this distance is longer at 2.477(3) Å. The two chloro ligands are in *anti* position with respect to each other.

Figure 2 shows the structure of the cation in crystals of $[L_3Mo_3O_4][Zn(Cl,Br)_4]_2 \cdot H_2O$ and the atom labeling scheme; Table 5 gives selected bond distances and angles. The trinuclear cation possesses the well known $\{Mo_3^{IV}O_4\}^{4+}$ cluster core [11, 12] where each Mo(IV) ion is capped by a tridentate amine ligand. The trinuclear cation is bisected by a crystallographic mirror plane; atoms O(1), O(3), Mo(2) and N(4) lie on this plane. The three five-membered chelate rings of the capping 1,4,7-triazacylcononane rings adopt either ($\lambda\lambda\lambda$) or ($\delta\delta\delta$) conformation. This is not compatible with crystallographic site symmetry *m*. A consequence of this is the unusually large thermal parameters of the carbon atoms C(7), C(8), and C(9) of the amine ligand at Mo(2) and physically meaningless carbon–carbon distances (C(9)–C(9a) 1.32(3); C(7)–C(8) 1.41(2) Å). This reflects the average of two positions for the carbon atoms. Attempts to refine the structure with a split atom model for these carbon atoms failed.

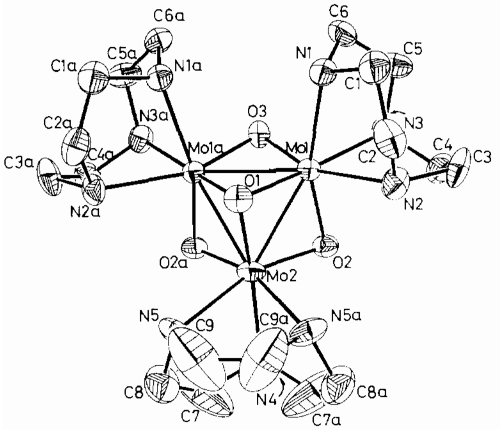


Fig. 2. Structure of the trinuclear cation in crystals of **6**.

TABLE 5. Selected bond lengths (Å) and angles (°) for $[L_3Mo_3O_4][Zn(Cl,Br)_4]_2 \cdot H_2O$

Mo(1)–Mo(2)	2.511(2)	Mo(1)–O(1)	2.084(8)
Mo(1)–O(2)	1.939(6)	Mo(1)–O(3)	1.918(8)
Mo(1)–N(1)	2.250(7)	Mo(1)–N(2)	2.246(9)
Mo(1)–N(3)	2.203(9)	Mo(1)–Mo(1a)	2.515(2)
Mo(2)–O(1)	2.054(10)	Mo(2)–O(2)	1.936(7)
Mo(2)–N(4)	2.177(11)	Mo(2)–N(5)	2.252(10)
Mo(2)–Mo(1a)	2.510(2)	Mo(2)–O(2a)	1.936(7)
Mo(2)–N(5a)	2.252(10)	O(1)–Mo(1a)	2.084(8)
O(3)–Mo(1a)	1.917(8)		
O(1)–Mo(1)–O(2)	100.3(4)	O(2)–Mo(1)–O(3)	99.2(4)
O(1)–Mo(1)–O(3)	100.7(3)	Mo(2)–Mo(1)–Mo(1a)	59.9(2)
O(1)–Mo(2)–O(2)	101.5(3)	O(2)–Mo(2)–O(2a)	99.4(4)
Mo(1)–Mo(2)–Mo(1a)	60.1(1)	Mo(1)–O(1)–Mo(1a)	74.3(3)
O(1)–Mo(2)–O(2a)	101.5(3)	Mo(1)–O(2)–Mo(2)	80.8(3)
Mo(1)–O(1)–Mo(2)	74.7(3)		
Mo(2)–O(1)–Mo(1a)	74.7(3)		
Mo(1)–O(3)–Mo(1a)	82.0(4)		
Average N–Mo–N	76.8	O–Mo–N	90.0

The geometrical properties of the $\{Mo_3O_4\}^{4+}$ core are very similar to those reported for many other complexes containing this unit but different terminal ligands [13].

Supplementary material

Tables of calculated positional parameters of H atoms, anisotropic thermal parameters and listings of F_o, F_c for **3** and **6** are available from author K.W.

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References

1 P. Schreiber, K. Wieghardt, B. Nuber and J. Weiss, *Z. Anorg. Allg. Chem.*, *587* (1990) 174.
2 P. S. Roy and K. Wieghardt, *Inorg. Chem.*, *26* (1987) 1885.
3 R. S. Taylor, P. Gans, P. F. Knowles and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, (1972) 24.
4 P. Schreiber, K. Wieghardt, B. Nuber and J. Weiss, *Z. Naturforsch., Teil B*, *45* (1990) 619.
5 P. Chaudhuri, K. Wieghardt, W. Gebert, I. Jibril and G. Huttner, *Z. Anorg. Allg. Chem.*, *521* (1985) 23.
6 *International Tables of X-ray Crystallography*, Vol. IV, Kynoch, Birmingham, UK, 1974, pp. 99 and 149.
7 P. Schreiber, K. Wieghardt, U. Flörke and H.-J. Haupt, *Inorg. Chem.*, *27* (1988) 2111.
8 K. Wieghardt, M. Hahn, W. Swiridoff and J. Weiss, *Angew. Chem., Int. Ed. Engl.*, *22* (1983) 491.

9 M. Hahn and K. Wieghardt, *Inorg. Chem., 23* (1984) 3977.
10 K. Wieghardt, M. Hahn, W. Swiridoff and J. Weiss, *Inorg. Chem., 23* (1984) 94.
11 A. Müller, R. Jostes and F. A. Cotton, *Angew. Chem., Int. Ed. Engl., 19* (1980) 875.
12 E. Benory, A. Bino, D. Gibson, F. A. Cotton and Z. Dori, *Inorg. Chim. Acta, 99* (1985) 137.
13 A. G. Sykes, in G. Wilkinson, R. D. Gillard and J. A. McCleverty (eds.), *Comprehensive Coordination Chemistry,* Vol. 3, Pergamon, Oxford, 1987, p. 1229.