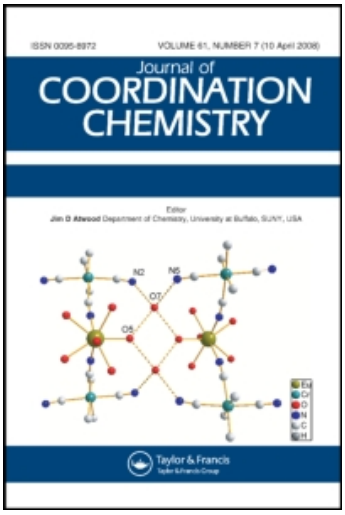

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DINUCLEAR METAL(O) COMPLEXES CONTAINING BRIDGING *OR* LIGANDS. SYNTHESIS, CRYSTAL STRUCTURE AND CYCLIC VOLTAMMETRY OF DINUCLEAR Mo AND W COMPLEXES, $[Et_4N]_3[M_2(CO)_6(\mu\text{-}OPh)_3]$ (M = Mo,W)

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The reaction of $M(CO)_6$ (M = Mo,W) with tetraethyl ammonium phenoxide affords the dinuclear M(O) complexes containing bridging *OR* ligands, $[Et_4N]_3[M_2(CO)_6(OPh)_3]$ (M = Mo (**1**), W (**2**)). The X-ray structures of **1** and **2** have been determined. **1**.3MeCN crystallizes in the monoclinic space group $P2_1/n$ with a = 11.971(5), b = 19.326(9), c = 26.492(8)Å; β = 102.26(3)°; V = 5989Å^3; Z = 4; R_1 = 0.083, R_2 = 0.098. **2**.2MeCN crystallizes in the orthorhombic space group $P2_12_12_1$ with a = 17.610(8), b = 26.712(15), c = 11.822(4)Å; V = 5561.2Å^3; Z = 4; R_1 = 0.058, R_2 = 0.087. The structures of both the anions of **1** and **2** possess three μ-OPh ligands and three terminal carbonyls on each M atom resulting in *pseudo*-C_{3v} symmetry. M-M distances are 3.315(3) and 3.3035(9)Å for **1** and **2**, respectively. The CV of **1** and **2** is discussed.

KEYWORDS: Mo and W complexes, bridging *OR* ligands, crystal structure, cyclic voltammetry.

INTRODUCTION

Recently, a series of dinuclear Mo(O) carbonyl complexes containing thiolate bridges, $[Mo_2(CO)_8(SR)_2]^{2-}$ (R = C_6H_5, *t*-Bu, Bz,[1–3] CH_2COOEt,[4] C_6H_4OH[5] and $CH_2C_6H_4$-CH_2SH)[6] have been synthesized and studied by our group. This series of Mo(O)-SR compounds possesses a common bimetallic MS_2M unit and exhibits a variety of redox chemistry and an interesting two-electron transfer character. This has prompted us to extend our attention to Mo(O) and W(O) complexes containing bridging oxygen atoms which may exhibit different chemistry and electrochemistry to the sulfur analogues. Mo(O)-*OR* and W(O)-*OR* complexes are rare in the literature. Although the dinuclear W(O) complex containing OH-bridges $[W_2(CO)_6(\mu\text{-}OH)_3]^{3-}$ was reported[7] twenty years ago, the W(O) complexes containing OR-bridges, $[W_2(CO)_6(\mu\text{-}OC_6H_5)_3]^{3-}$[8,9] and $[W_2(CO)_8(\mu\text{-}OCH_2CF_3)_2]^{2-}$,[8] were not synthesized until 1982 and 1990, respectively, and their X-ray crystal structures were not presented until later. The Mo(O) analogue seems not to be reported so

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far. We herein report the synthesis, structure and preliminary electrochemistry of the dinuclear Mo(W)(O) carbonyl complexes containing oxy-bridges $[Et_4N]_3[M_2(CO)_6(\mu\text{-}OPh)_3]$ (M = Mo (**1**), W(**2**)).

EXPERIMENTAL

Materials and methods

Molybdenum hexacarbonyl and tungsten hexacarbonyl were purchased from Alfa. Acetonitrile was distilled from CaH_2 and 2-propanol was dried by distillation from magnesium methoxide. All synthetic reaction procedures, crystal growth and preparation of the samples for X-ray determination and cyclic voltammetry were carried out under dinitrogen using the Schlenk technique and degassed solvents. All reactants were degassed before use.

Synthesis of $[Et_4N]_3[M_2(CO)_6(\mu\text{-}OPH)_3]$ (M = Mo (1), W(2))

Reaction of $M(CO)_6$ (5 mmol) with Et_4NOPh (5 mmol) (prepared by reaction of ET_4NCl with NaOPh in MeCN) in MeCN at 45°C for 24 h resulted in light brown solution. After concentration and addition of isopropanol, yellow crystalline products (1.2 g for **1** and 0.7 g for **2**) were obtained by filtering, washing and drying *in vacuo*. The yeilds are 70 and 35% for **1** and **2** respectively (based on Et_4NOPh used). Analysis for **1**, calcd. for $C_{98}H_{75}O_9N_3Mo_2$: C, 55.98; H, 7.29; N, 4.08; Mo, 18.66%. Found:C, 55.75; H, 7.30; N, 4.35; Mo, 18.10%; IR (KBr pellet): 1930_{sh}, 1872s, 1720s cm^{-1} (ν_{MoC-O}). For **2**, calcd. for $C_{48}H_{75}O_9N_3W_2$: C, 47.80; H, 6.22; N, 3.49; W, 30.50%. Found: C, 47.55; H, 6.23; N, 3.60; W, 29.50%; IR (KBr pellet): 1920sh, 1860s, 1718s cm^{-1} (ν_{WC-O}).

Reaction of 1 with Et_4NSPh

An Et_4NSPh solution prepared from the reaction of NaSPh (0.132 g) with ET_4NCl (0.166 g) in 50 cm^3 MeCN at 50°C for 24 h was added to solid **1** (1.03 g), and the resulting mixture was stirred at 50°C for 24 h, resulting in a yellow-green solution. After concentration and removal of unreacted **1**, 0.2 g of a yellow, microscrystalline product, obtained by filtering, washing with *i*-PrOH and drying under vacuum, was recognized as $[Et_4N]_2[Mo_2(CO)_8(SPh)_2]$[2] from its IR spectrum.

Electrochemical measurements

Cyclic voltammetry (CV) experiments were carried out with a three electrode cell using 0.1 M Et_4NBF_4 as supporting electrolyte and MeCN as solvent. The working electrode was glassy carbon, the reference electrode an aqueous SCE separated from the sample solution by a salt bridge and the auxiliary electrode Pt. Solutions were deoxygenated and blanketed with nitrogen. The potentiostat used was a model CV-1B from Bioanalytical Systems.

Determination of the X-ray crystal structures

The X-ray crystallography experiments were performed with MoKα radiation (λ = 0.71069Å) on a MSC/Rigaku diffractometer and all calculations were carried out on a VAX computer using SDP/VAX. A total of 11438 (for **1** .3MeCN) and 7106 (for **2**.2MeCN) reflections were collected using the $\omega - 2\theta$ scan technique. Lorentz and polarization corrections and an empirical absorption correction based on a series of psi-scans were applied to the data. The linear absorption coefficient is 4.6 cm^{-1} (for **1**.3MeCN) and 42.8 cm^{-1} (for **2**.2MeCN) and the relative transmission coefficients ranged from 0.843 to 0.999 and from 0.747 to 0.896 for **1**.3MeCN and **2**.2MeCN, respectively. An empirical absorption correction by the program DIFABS was made after structure refinement with isotropic thermal parameters. The max. and min. absorption corrections were 1.3984 and 0.4766, respectively, for **1**.3MeCN and 1.2680 and 0.7092, respectively, for **2**.2MeCN.

Both the structures of **1**.3MeCN and **2**.2MeCN were solved by direct methods. A total of 5 atoms were located from an E-map at first, and the remaining atoms were located in subsequent difference Fourier syntheses. For **1**.3MeCN, H atoms were not included in the calculations and for **2**.2MeCN, H atoms were located and added to the structure factor calculations although their positions were not refined. The structures were refined using full-matrix least-squares methods where the function minimized was $\Sigma W(|Fo|-|Fc|)^2$ with the weight w defined as per the Killer and Lawrence method with terms of 0.020 and 1.0. The final cycle of refinement for **1**.3MeCN included 425 variable parameters for 3239 reflections ($I>3\sigma(I)$) and converged to 0.05σ with R_1 = 0.083 and R_2 = 0.098; for **2**.2MeCN, the final cycle of refinement included 583 variable parameters for 5179 reflections ($I3\sigma(I)$) and converged to 1.31σ with R_1 = 0.058 and R_2 = 0.087. The e.s.d.s of observations of unit weight are 1.27 and 1.95 for **1**.3MeCN and **2**.2MeCN respectively. The highest peaks in the final difference Fouriers had were of 1.05e/Å^2 and 1.42e/Å^3 for **1**.3MeCN and **2**.2MeCN respectively. Crystal data for **1**.3MeCN are $C_{54}H_{8\ 4}N_6O_9Mo_2$, M = 1153.10, monoclinic, space group $P2_1/n$ (No. 14), a = 11.971(5), b = 19.326(9), c = 26.492(8)Å, β = 102.26(3)°, V = 5989Å^3, Z = 4, D_c = 1.28g/cm^3, R_1 = 0.083, R_2 = 0.098; for **2**.2MeCN, $C_{5\ 2}H_{8\ 1}N_5O_9W_2$, M = 1287.95, orthorhombic, space group $P2_12_12_1$ (No. 19), a = 17.610(8), b = 26.712(15), c = 11.822(4)Å, V = 5561Å^3, Z = 4, D_c = 1.54g/cm^3, R_1 0.058, R_2 = 0.087. Final positional and thermal parameters with e.s.d.s are listed in Tables 1 and 2.

RESULTS AND DISCUSSION

Reaction of the metal hexacarbonyl with tetraethylammonium phenoxide in acetonitrile at 45°C affords $[Et_4N]_3[M_2(CO)_6(OPh)_3]$. It seems that in contrast with the reaction with thiolate, which tends to give dinuclear compounds with two briding SR ligands, the reaction with phenoxide leads to three bridging *OR*-containing dinuclear complexes in spite of the use of a 1:1 ratio of $M(CO)_6$:OPh. This is obviously related to the radius and electronegativity of the bridging atoms, oxygen and sulfur. Therefore, it is possible to form the product

Table I Positional Parameters for **1**.3MeCN.

Atom	*x/a*	*y/b*	*z/c*	B(Å^2)
Mo(1)	0.8640(2)	0.21922(9)	0.79626(7)	3.27(4)
Mo(2)	1.0863(2)	0.23820(9)	0.89399(6)	3.17(4)
O(1)	0.643(1)	0.1351(8)	0.7858(6)	6.1(4)
O(2)	0.686(2)	0.3266(7)	0.7421(6)	6.4(5)
O(3)	0.851(2)	0.1736(9)	0.6836(5)	8.4(6)
O(4)	1.161(2)	0.1589(9)	0.9958(6)	7.3(5)
O(5)	1.167(2)	0.3599(8)	0.9663(6)	8.3(6)
O(6)	1.351(1)	0.2269(9)	0.9008(5)	6.4(4)
O(10)	1.025(1)	0.2871(6)	0.8161(4)	3.7(3)
O(20)	1.009(1)	0.1517(6)	0.8406(4)	3.2(3)
O(30)	0.905(1)	0.2503(7)	0.8825(5)	4.8(3)*
C(1)	0.735(2)	0.162(1)	0.7929(9)	7.2(7)*
C(2)	0.765(2)	0.288(1)	0.7633(7)	3.8(4)*
C(3)	0.865(2)	0.188(1)	0.7263(8)	4.9(5)*
C(4)	1.133(2)	0.187(1)	0.9557(7)	4.3(5)*
C(5)	1.138(2)	0.315(1)	0.9376(7)	4.0(5)*
C(6)	1.228(1)	0.2309(8)	0.8889(6)	2.2(3)*
C(11)	1.0749(8)	0.3310(4)	0.7880(3)	3.1(4)*
C(12)	1.0326(0)	0.3362(0)	0.7361(0)	3.6(4)*
C(13)	1.0854(0)	0.3794(0)	0.7081(0)	5.5(6)*
C(14)	1.1781(0)	0.4163(0)	0.7326(0)	4.5(5)*
C(15)	1.2195(0)	0.4100(0)	0.7852(0)	5.5(6)*
C(16)	1.1667(0)	0.3664(0)	0.8135(0)	4.5(5)*
C(21)	1.0289(8)	0.0769(5)	0.8391(3)	4.2(5)*
C(22)	0.9472(0)	0.0346(0)	0.8137(0)	3.7(5)*
C(23)	0.9773(0)	-0.0325(0)	0.8151(0)	5.1(5)*
C(24)	1.0840(0)	-0.0479(0)	0.8411(0)	4.9(5)*
C(25)	1.1646(0)	-0.0034(0)	0.8662(0)	4.6(5)*
C(26)	1.1375(0)	0.0652(0)	0.8659(0)	4.5(5)*
C(31)	0.8251(9)	0.2753(4)	0.9106(3)	4.9(5)*
C(32)	0.8700(0)	0.2987(0)	0.9608(0)	4.6(5)*
C(33)	0.7924(0)	0.3160(0)	0.9896(0)	7.0(7)*
C(34)	0.6784(0)	0.3121(0)	0.9715(0)	6.1(6)*
C(35)	0.6346(0)	0.2885(0)	0.9224(0)	7.2(7)*
C(36)	0.7125(0)	0.2717(0)	0.8936(0)	3.2(4)*
N(4)	1.277(2)	0.1729(8)	0.7255(5)	4.8(5)
C(41)	1.161(2)	0.157(1)	0.7407(7)	3.9(5)
C(42)	1.111(2)	0.090(1)	0.7162(8)	5.4(6)
C(43)	1.262(2)	0.175(1)	0.6663(7)	4.4(6)
C(44)	1.189(2)	0.234(1)	0.6401(8)	6.2(7)
C(45)	1.361(2)	0.116(1)	0.7427(8)	4.4(5)
C(46)	1.385(2)	0.103(1)	0.8020(8)	6.4(7)
C(47)	1.313(2)	0.242(1)	0.7539(8)	4.6(5)
C(48)	1.428(2)	0.267(1)	0.7462(9)	6.1(7)
N(5)	0.715(2)	0.0567(8)	0.9479(6)	5.0(4)*
C(51)	0.704(2)	-0.020(1)	0.9389(7)	5.3(5)*
C(52)	0.675(2)	-0.036(1)	0.8765(8)	6.5(6)*
C(53)	0.608(2)	0.098(1)	0.9240(9)	8.0(7)*
C(54)	0.497(3)	0.069(1)	0.9376(9)	8.9(8)*
C(55)	0.817(2)	0.090(1)	0.9259(8)	6.8(6)*
C(56)	0.926(3)	0.053(1)	0.9478(9)	9.0(8)*
C(57)	0.737(2)	0.059(1)	1.0076(8)	6.0(6)*
C(58)	0.765(2)	0.138(1)	1.0264(9)	7.4(7)*
N(6)	0.840(2)	0.4882(8)	0.8646(6)	5.1(4)*
C(61)	0.745(3)	0.431(1)	0.8527(9)	8.7(8)*

Table 1 *Continued*

Atom	*x/a*	*y/b*	*z/c*	B(Å^2)
C(62)	0.625(3)	0.458(1)	0.8329(9)	8.9(8)*
C(63)	0.956(3)	0.456(1)	0.885(1)	9.4(8)*
C(64)	1.056(3)	0.512(2)	0.893(1)	14(1)*
C(65)	0.847(2)	0.532(1)	0.8129(9)	8.3(7)*
C(66)	0.877(2)	0.478(1)	0.7731(8)	7.0(6)*
C(67)	0.815(2)	0.547(1)	0.8997(9)	8.2(7)*
C(68)	0.790(3)	0.510(1)	0.950(1)	9.9(8)*
N(7)	0.493(2)	0.145(1)	1.0618(8)	9.5(6)*
C(71)	0.444(3)	0.200(1)	1.053(1)	9.7(8)*
C(72)	0.397(3)	0.266(2)	1.038(1)	10.8(9)*
N(8)	1.424(2)	0.555(1)	0.9273(9)	11.8(8)*
C(81)	1.399(3)	0.496(2)	0.929(1)	11(1)*
C(82)	1.047(3)	0.425(1)	0.9376(9)	8.9(8)*
N(9)	1.020(3)	0.303(1)	1.121(1)	14.3(9)*
C(91)	1.068(2)	0.257(1)	1.1176(9)	8.9(7)*
C(92)	0.641(3)	0.297(2)	0.617(1)	11.3(9)*

* Starred atoms were refined istropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)*[a^2*\beta(1,1) + b^2*\beta(2,2) + c^2*\beta(3,3) + ab(\cos\lambda)*\beta(1,2) + ac(\cos\beta)*\beta(1,3) + bc(\cos\alpha)*\beta(2,3)]$.

Table 2 Positional Parameters for **2**.2MeCN.

Atom	*xa*	y/*b*	*z/c*	*B*(Å2)
W(1)	0.85140(5)	0.13638(3)	0.84148(7)	2.54(1)
W(2)	0.83845(6)	0.23790(3)	0.68306(7)	2.99(2)
O(1)	0.855(1)	0.0231(6)	0.776(2)	5.7(5)
O(2)	0.753(1)	0.0978(8)	1.040(2)	6.6(5)
O(3)	0.987(1)	0.1006(7)	0.991(2)	5.1(4)
O(4)	0.816(1)	0.2387(8)	0.424(1)	6.7(5)
O(5)	0.731(1)	0.3313(7)	0.694(2)	5.8(5)
O(6)	0.955(1)	0.3213(6)	0.642(2)	6.2(5)
O(10)	0.8536(8)	0.2200(5)	0.863(1)	2.8(3)
O(20)	0.9126(8)	0.1712(5)	0.695(1)	2.9(3)
O(30)	0.7680(9)	0.1721(6)	0.729(1)	3.5(3)
C(1)	0.848(1)	0.0666(8)	0.798(2)	3.0(4)
C(2)	0.789(1)	0.1143(8)	0.962(2)	3.4(5)
C(3)	0.934(1)	0.1147(9)	0.935(2)	3.3(5)
C(4)	0.824(2)	0.238(1)	0.521(2)	6.4(8)
C(5)	0.772(2)	0.296(1)	0.689(2)	4.3(6)
C(6)	0.911(1)	0.2896(8)	0.657(2)	3.9(5)
C(11)	0.863(1)	0.2495(8)	0.953(2)	3.2(4)
C(12)	0.860(1)	0.2307(9)	1.064(2)	4.0(5)
C(13)	0.868(2)	0.260(1)	1.157(2)	5.6(7)
C(14)	0.881(2)	0.310(1)	1.142(2)	5.7(7)
C(15)	0.884(2)	0.332(1)	1.035(3)	6.5(8)
C(16)	0.874(1)	0.302(1)	0.943(2)	4.4(6)
C(21)	0.974(2)	0.1559(9)	0.635(2)	4.2(5)
C(22)	1.010(1)	0.1100(8)	0.654(2)	3.9(5)
C(23)	1.074(2)	0.090(2)	0.583(3)	8.4(9)
C(24)	1.100(2)	0.119(1)	0.503(3)	7.3(8)
C(25)	1.063(2)	0.165(1)	0.484(2)	8.3(8)
C(26)	0.998(2)	0.1851(9)	0.545(2)	4.7(6)

Table 2 *Continued*

Atom	*xa*	y/*b*	*z*/*c*	*B*(Å2)
C(31)	0.695(1)	0.1623(8)	0.702(2)	3.3(5)
C(32)	0.651(1)	0.1250(9)	0.766(2)	4.7(6)
C(33)	0.578(2)	0.117(1)	0.735(3)	7.0(9)
C(34)	0.541(2)	0.140(1)	0.649(3)	7.6(8)
C(35)	0.581(2)	0.175(1)	0.593(3)	5.4(7)
C(36)	0.657(2)	0.187(1)	0.613(2)	5.6(6)
N(4)	0.383(1)	0.7638(8)	0.463(2)	4.0(4)
C(41)	0.353(1)	0.7096(9)	0.473(2)	4.5(6)
C(42)	0.415(2)	0.669(1)	0.453(4)	8(1)
C(43)	0.449(2)	0.775(1)	0.547(3)	5.4(7)
C(44)	0.421(2)	0.770(2)	0.672(3)	10(1)
C(45)	0.314(2)	0.798(1)	0.483(4)	10(1)
C(46)	0.334(3)	0.856(1)	0.465(5)	14(2)
C(47)	0.421(2)	0.772(1)	0.349(3)	8.1(8)
C(48)	0.361(3)	0.761(2)	0.251(3)	12(1)
N(5)	0.311(1)	0.4315(8)	0.599(2)	5.0(5)
C(51)	0.251(2)	0.423(1)	0.685(3)	7.4(9)
C(52)	0.216(2)	0.372(2)	0.677(3)	10(1)
C(53)	0.341(3)	0.485(1)	0.620(3)	9(1)
C(54)	0.399(2)	0.504(1)	0.531(3)	10(1)
C(55)	0.289(2)	0.427(1)	0.483(3)	8(1)
C(56)	0.222(2)	0.464(2)	0.455(3)	10(1)
C(57)	0.381(2)	0.392(1)	0.615(3)	9(1)
C(58)	0.426(3)	0.401(2)	0.738(4)	13(1)
N(6)	0.409(1)	0.0347(6)	0.339(2)	4.7(5)
C(61)	0.358(2)	0.074(1)	0.294(3)	6.5(8)
C(62)	0.321(3)	0.063(1)	0.179(4)	10(1)
C(63)	0.429(2)	0.054(1)	0.451(4)	9(1)
C(64)	0.486(3)	0.023(2)	0.513(4)	13(1)
C(65)	0.471(3)	0.025(1)	0.261(4)	10(1)
C(66)	0.514(2)	0.068(1)	0.231(4)	10(1)
C(67)	0.368(2)	-0.0154(8)	0.351(4)	10(1)
C(68)	0.299(3)	-0.014(2)	0.429(4)	13(1)
N(7)	0.782(3)	0.442(2)	0.318(4)	14(1)*
C(71)	0.775(3)	0.410(2)	0.361(4)	10(1)*
C(72)	0.789(2)	0.354(1)	0.414(3)	9(1)*
N(8)	0.601(5)	0.509(3)	0.599(7)	12(3)*
C(81)	0.599(4)	0.500(2)	0.666(6)	6(1)*
C(82)	0.616(4)	0.462(3)	0.747(6)	8(2)*

Starred atoms and *B* as in Table 1.

containing two bridging *OR* ligands, if an *R* group which decreases the electronegativity of the oxygen atom is used. As a matter of fact, $[W_2(CO)_8(OR)_2]^{3-}$ was obtained when R is CH_2CF_3.[10] No triple *SR*-bridged compound, but rather a double *SR*-bridged compound $[Mo_2(SR)_2(CO)_8]^{2-}$ was isolated when $[Mo_2(CO)_6(OR)_3]^{3-}$ was reacted with Et_4NSR in MeCN. The same result was obtained when $Mo(CO)_3(MeCN)_3$ was used instead of $[Mo_2(CO)_6(OR)_3]^{3-}$ to react with Et_4NSR, although an $Mo(CO)_3$ fragment was provided in the reaction. The yield for W was lower than that of Mo; this is consistent with the fact that tungsten carbonyls are generally more inert towards substitution than molybdenum compounds.[10-11] Selected bond distances and angles in **1**.3MeCN and **2**.2MeCN are listed in Tables 3 and 4, and the structure of the anions of **1** and

Table 3 Selected Bond Distances (Å) of the Anions of **1** and **2**.

M = Mo W	1.3MeCN	2.2MeCN
M(1)-M(2)	3.315(3)	3.3035(9)
M(1)-O(10)	2.30(1)	2.25(1)
M(1)-O(20)	2.29(1)	2.24(2)
M(1)-O(30)	2.31(1)	2.20(1)
M(2)-O(10)	2.24(1)	2.20(1)
M(2)-O(20)	2.26(2)	2.21(2)
M(2)-O(30)	2.14(1)	2.22(1)
M(1)-C(1)	1.88(3)	1.94(2)
M(1)-C(2)	1.86(2)	1.89(2)
M(1)-C(3)	1.95(3)	1.92(2)
M(2)-C(4)	1.90(3)	1.93(2)
M(2)-C(5)	1.90(2)	1.94(2)
M(2)-C(6)	1.74(2)	1.91(2)
O(1)-C(1)	1.20(3)	1.20(2)
O(2)-C(2)	1.25(3)	1.20(2)
O(3)-C(3)	1.14(2)	1.21(2)
O(4)-C(4)	1.17(3)	1.15(2)
O(5)-C(5)	1.16(2)	1.19(2)
O(6)-C(6)	1.44(2)	1.17(2)
O(10)-C(11)	1.35(1)	1.33(2)
O(20)-C(21)	1.47(1)	1.36(2)
O(30)-C(31)	1.42(1)	1.35(3)
C(11)-C(12)	1.364(8)	1.41(2)
C(11)-C(16)	1.347(9)	1.42(2)
C(12)-C(13)	1.359(3)	1.38(3)
C(13)-C(14)	1.362(3)	1.39(3)
C(14)-C(15)	1.381(4)	1.38(3)
C(15)-C(16)	1.368(4)	1.36(3)
C(21)-C(22)	1.35(1)	1.40(3)
C(21)-C(26)	1.37(1)	1.38(3)
C(22)-C(23)	1.344(3)	1.49(3)
C(23)-C(24)	1.349(4)	1.30(3)
C(24)-C(25)	1.356(4)	1.42(4)
C(25)-C(26)	1.366(4)	1.45(3)
C(31)-C(32)	1.399(9)	1.47(2)
C(31)-C(36)	1.33(2)	1.40(2)
C(32)-C(33)	1.364(1)	1.35(3)
C(33)-C(34)	1.349(1)	1.36(4)
C(34)-C(35)	1.374(1)	1.36(4)
C(35)-C(36)	1.363(3)	1.41(3)

2 are depicted in Figures 1 and 2. As shown in Tables 1–4 and the figures, the structures of the anions of both compounds are very similar and contain two essentially octahedral metal centres with the geometry at each centre being a *facial* $(CO)_3MO_3$ fragment (M = Mo, W), this resulting in a bimetallic MO_3M core. There is a *pseudo*-C_{3v} axis through the two metal atoms. M-O-M angles of 94.6° (average) and 96.2° (average) for **1** and **2**, respectively, bring about close contact between the two metal atoms with Mo...Mo 3.315(3)Å and W...W 3.304(1)Å. Average metal-oxygen bond lengths are 2.25Å (Mo-O) and 2.22Å (W-O) and the average M-C bond distances are 1.87Å (Mo-C) and 1.92Å (W-C). These are comparable with those observed in the $(CO)_3MO_3$ compounds, $[Et_4N]_2[Mo_2(CO)_3(S,O\text{-}C_6H_4\text{-}1,2)_3]^{2-}$ (Mo-O, 2.25Å; Mo-C, 1.90Å)[12] and

Table 4 Selected Bond Angles (°) for the Anions of **1** and **2**.

	1.3MeCN	**2**.2MeCN
M(1)-O(10)-M(2)	93.7(4)	96.0(4)
M(1)-O(20)-M(1)	93.8(4)	95.8(4)
M(1)-O(30)-M(1)	96.3(5)	96.8(4)
O(10)-M(1)-O(20)	72.5(4)	70.5(4)
O(10)-M(1)-O(30)	68.6(4)	69.4(5)
O(10)-M(2)-O(20)	74.1(4)	72.0(4)
O(10)-M(2)-O(30)	72.6(5)	70.0(4)
O(20)-M(2)-O(30)	74.0(4)	71.1(4)
O(10)-M(1)-C(1)	169.7(8)	170.8(5)
O(20)-M(1)-C(2)	169.4(6)	103.6(6)
O(30)-M(1)-C(3)	167.5(8)	102.7(6)
O(10)-M(2)-C(4)	173.1(6)	167.5(7)
O(20)-M(2)-C(5)	174.9(8)	102.1(6)
O(30)-M(2)-C(6)	167.5(6)	103.4(7)
M(1)-C(1)-O(1)	168(2)	171(1)
M(1)-C(2)-O(2)	170(2)	176(2)
M(1)-C(3)-O(3)	171(3)	179(2)
M(2)-C(4)-O(4)	175(2)	178(2)
M(2)-C(5)-O(5)	176(2)	179(1)
M(2)-C(6)-O(6)	163(1)	179(1)
M(1)-O(10)-C(11)	132.8(8)	132.8(9)
M(2)-O(10)-C(11)	132.7(8)	131(1)
O(10)-C(11)-C)12)	119.4(8)	122(1)
O(10)-C(11)-C(16)	116.8(8)	122(2)
C(11)-C(12)-C(133)	118.7(4)	116(2)
C(12)-C(13)-C(14)	119.13(3)	123(2)
C(13)-C(14)-C(15)	121.15(4)	118(2)
C(14)-C(15)-C(16)	119.80(4)	122(2)
C(11)-C(16)-C(15)	117.5(3)	123(2)
C(12)-C(11)-C(16)	123.7(6)	116(2)
M(1)-O(20)-C(21)	131.2(7)	131(2)
M(2)-O(20)-C(21)	134.4(7)	133(2)
O(20)-C(21)-C(22)	120.5(8)	123(2)
O(20)-C(21)-C(26)	107.0(7)	118(2)
C(22)-C(21)-C(26)	132.4(6)	119(2)
C(21)-C922)-C(23)	114.3(4)	125(2)
C(22)-C(23)-C(24)	116.44(8)	117(3)
C(23)-C(24)-C(25)	127.53(6)	118(3)
C(24)-C(25)-C(26)	117.99(7)	127(2)
C(21)-C(26)-C(25)	111.3(3)	114(3)
M(1)-O(30)-C(31)	125.6(9)	135(2)
M(2)-O(30)-C(31)	137.8(8)	129(2)
O(30)-C(31)-C(32)	116.4(9)	121(2)
O(30)-C(31)-C(36)	123.6(8)	122(2)
C(32)-C(31)-C(36)	119.8(6)	117(2)
C(31)-C(32)-C(33)	116.2(5)	119(2)
C(32)-C(33)-C(34)	123.07(9)	127(3)
C(33)-C(34)-C(35)	120.61(4)	116(2)
C(34)-C(35)-C(36)	116.08(5)	124(2)
C(31)-C(36)-C(35)	124.3(4)	119(2)
M(1)-M(2)-O(10)	43.9(3)	42.6(3)
M(1)-M(2)-O(20)	43.5(3)	42.5(3)
M(1)-M(2)-O(30)	43.9(4)	41.3(3)

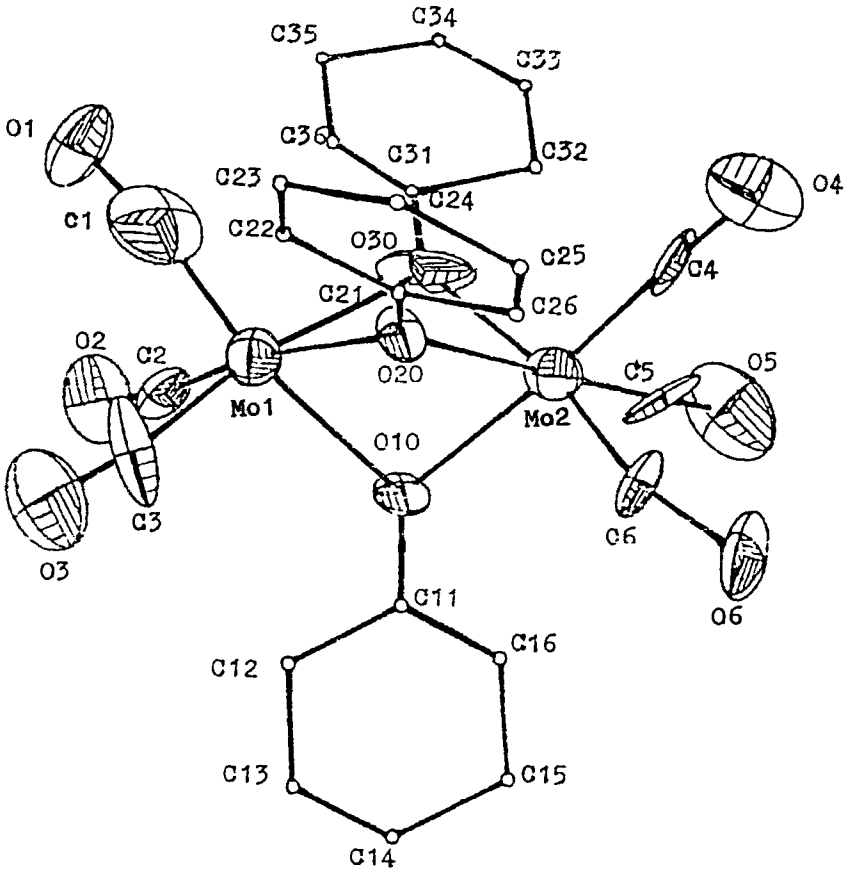

Figure 1 The molecular structure of the anion of **1** showing the atom numbering scheme and 50% probability thermal ellipsoids.

$[Et_4N]_3[W_2(CO)_6(Oph)_3]$.3MeCN (W-O, 2.222Å; W-C, 1.904Å).[8] By carefully comparing **2**.2MeCN with $[Et_4N]_3[W_2(CO)_6(OPh)_3]$.3MeCN, it can be found that the structural parameters of the anion of both crystal forms are identical, although the number of solvate molecules are different. However, it is worth noting that crystals of **1**.3MeCN are isostructural with $[Et_4N]_3[W_2(CO)_6(OPh)_3$.3MeCN as reported by Darensbourg[8] in terms of similar lattice constants and similar positions of metal in the lattices.

Cyclic voltammograms of **1** and **2** in MeCN are shown in Figure 3 and potentials are listed in Table 5. The electrochemistry of the two complexes is very similar. The *pseudo*-reversible redox couple at − 0.42 V *vs* SCE and an irreversible oxidation at − 0.10 V *vs* SCE are almost the same for both complexes; another *pseudo*-reversible redox couple at positive potentials for the Mo compound has a 70–90 mV *vs* SCE more positive shift than that of the W-compound. This obviously implies the existence of a chemical reaction in the electrode reaction process. In terms of the fact that $[M_2(OR)_3(CO)_6]^{3-}$ reacts with ^-SR resulting in $[M_2(SR)_2(CO)_8]^{2-}$ and

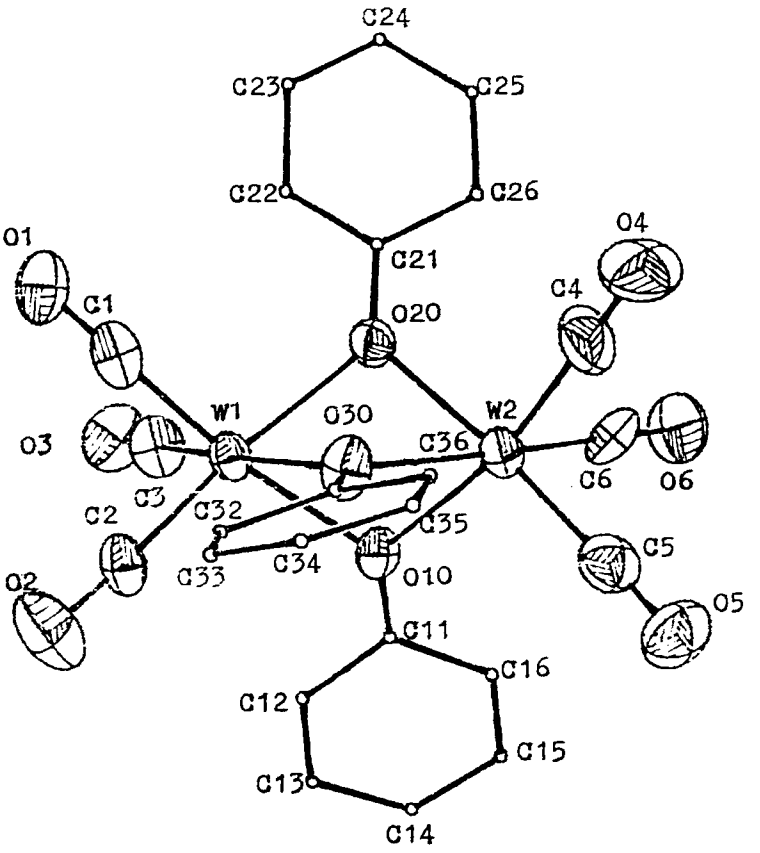

Figure 2 The moleculare structure of the anion of **2** showing the atom numbering scheme and 50% probability thermal ellipsoids.

Table 5 Redox Potentials for **1** and **2** in MeCN (V *vs* SCE).

		1	2
Couple 1	E_{PC}	−0.48	−0.5
	E_{Pa}	−0.35	−0.35
	$E_{1/2}$[a]	−0.42	−0.43
Couple 2	E_{PC}	+0.25	+0.15
	E_{PA}	+0.35	+0.27
	$E_{1/2}$	+0.30	+0.21
Couple 3	E_{PC}	+0.60	+0.52
	E_{Pa}	+0.70	+0.63
	$E_{1/2}$	+0.65	+0.58
Ox. peak	E_{Pa}	+0.10	+0.12

[a] $E_{1/2} = (E_{Pa} + E_{Pc})/2$.

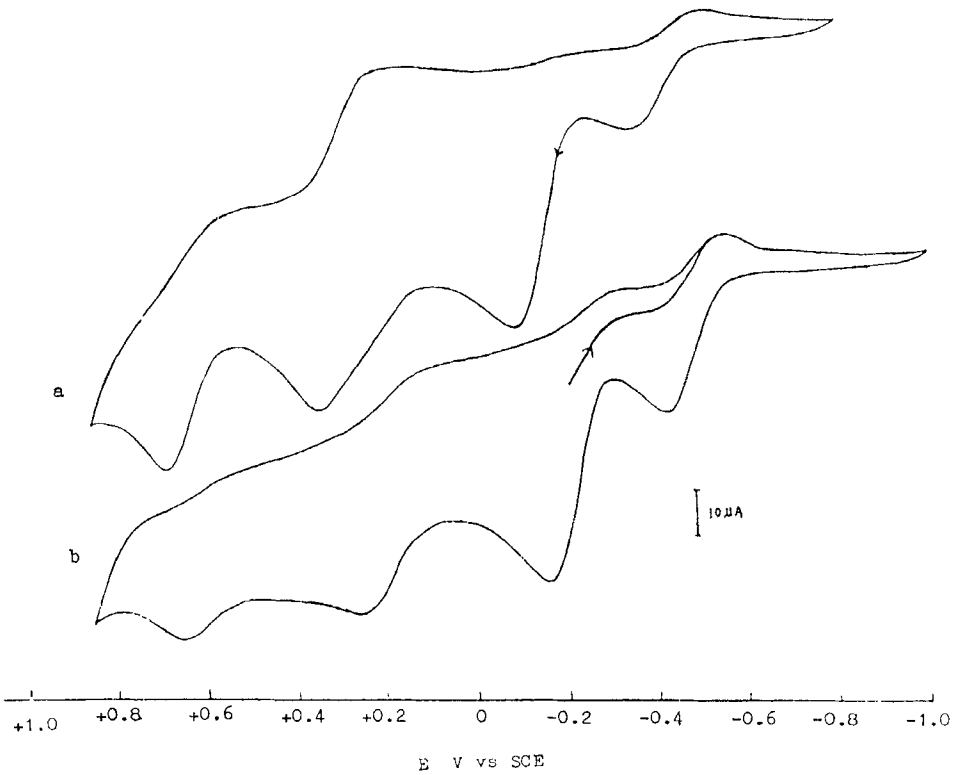

Figure 3 Cyclic voltammogram of $[Et_4N]_3[M_2(CO)_6(OPh)_3]$ in MeCN, a, M = Mo; b, M = W. Scan rate: 200 mv/s, concentration: 0.002 M.

referring to electrochemical data for the double bridging *SR* complexes $[M_2(SR)_2(CO)_8]^{2-}$ (M = Mo, W) (redox potential at −0.4 V *vs* SCE[2-3]), it is suggested that an equilibrium (*A*) between triple bridging *OR* complex and double bridging *OR* compound exists in solution in the presence of CO generated from the chemical reaction of $[M_2(OR)_3(CO)_6]^{3-}$ in the electrode reaction process.

$$[M_2(OR)_3(CO)_6]^{3-} + 2CO \leftrightarrows [M_2(CO)_8(OR)_2]^{2-} + {}^{-}OR \quad (A)$$

The redox couple at −0.4 V *vs* SCE reasonably results from the redox of $[M_2(OR)_2(CO)_8]^{2-}$ and the redox couples at positive potentials may be assigned to the reaction of triple bridging *OR* compounds, $[M_2(OR)_3(CO)_6]^{3-}$. The irreversible oxidation peak at −0.1V is thought to involve some decomposition product.

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Supplementary material

Full lists of bond lengths and angles, hydrogen positions temperature factors and observed and calculated structure factors are available from authors on request.

References

1. B. Zhuang, L.R. Huang, L.J. He, Y. Yang and J. X. Lu, *Inorg. Chim. Acta*, **157**, 85 (1989).
2. B. Zhuang, J.W. McDonald, F.A. Schultz and W.E. Newton, *Organometallics*, **3**, 943 (1984).
3. D.M. Smith, B. Zhuang, W.E. Newton, J.W. McDonald and F.A. Schultz, *Inorg. Chem.*, **26**, 2524 (1987).
4. B. Zhuang, L.R. Huang, L.J. He, W. Z. Chen, Y. Yang and J.X. Lu, *Acta Chinica Sinica*, **4**, 294 (1986).
5. B. Zhuang, L. R. Huang, J.X. Lu, *Jiegou Huaxue*, **8**, 103 (1989).
6. L. R. Huang, B. Zhuang, J. X. Ju, *Jiegou Huaxue*, **8**, 19 (1989).
7. V. G. Albano, G. Ciani and M. Manassero, *J. Organomet. Chem.*, **25**, C55 (1970).
8. D.J. Darensbourg, B.L. Mueller, C.J. Bischoff, C.C. Johnson, K.M. Sarchez, M. Kathoyn and J. H. Reibenspies, *Isr. J. Chem.*, **30**, 369 (1990).
9. J. E. Ellis and G.L. Rochfort, *Organometallics*, **1**, 682 (1982).
10. B, Zhuang, J.W. McDonald, F.A. Schultz and W.E. Newton, *Inorg. Chim. Acta*, **99**, L29 (1985).
11. B. Zhuang, P. Yu, L.R. Huang, L.J. He and J.X. Lu, *Inorg. Chim. Acta*, '**177**, 239 (1990).
12. B. Zhuang, L. Huang, L. He, P. Yu, A. Lan and J. Lu, *Inorg. Chim. Acta*, **179**, 178 (1991).