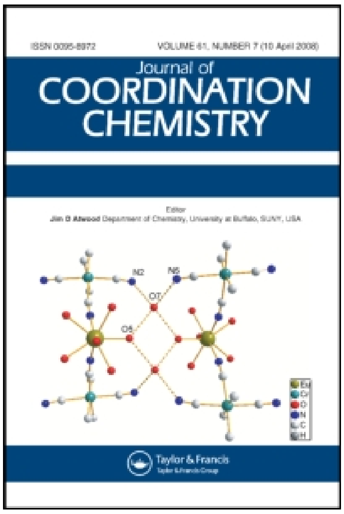

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Syntheses and crystal structures of quadruply bridged Mo_2Se_4 complexes containing functionalized cyclopentadienyl ligands: *trans/anti* - (η^5-$CH_3O_2CC_5H_4)_2Mo_2(\mu$-Se$)_2(\mu$-SeCH$_2$Ph)($\mu$-SePh) and *trans/syn*-($\eta^5$-$C_2H_5O_2CC_5H_4)_2Mo_2(\mu$-Se$)_2(\mu$-SePh$)_2$

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SYNTHESES AND CRYSTAL STRUCTURES OF QUADRUPLY BRIDGED Mo_2Se_4 COMPLEXES CONTAINING FUNCTIONALIZED CYCLOPENTADIENYL LIGANDS: *trans/anti*-$(\eta^5\text{-}CH_3O_2CC_5H_4)_2Mo_2(\mu\text{-}Se)_2(\mu\text{-}SeCH_2Ph)(\mu\text{-}SePh)$ AND *trans/syn*-$(\eta^5\text{-}C_2H_5O_2CC_5H_4)_2Mo_2(\mu\text{-}Se)_2(\mu\text{-}SePh)_2$

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Two quadruply bridged Mo_2Se_4 complexes trans/anti-$(\eta^5\text{-}CH_3O_2CC_5H_4)_2Mo_2(\mu\text{-}Se)_2(\mu\text{-}SeCH_2Ph)(\mu\text{-}SePh)$ (**1**) from reaction of $(\eta^5\text{-}CH_3O_2CC_5H_4)_2Mo_2(CO)_4$ with dibenzyldiselenide and trans/syn-$(\eta^5\text{-}C_2H_5O_2CC_5H_4)_2Mo_2(\mu\text{-}Se)_2(\mu\text{-}SePh)_2$ (**2**) from reaction of $(\eta^5\text{-}C_2H_5O_2CC_5H_4)_2Mo_2(CO)_2(\mu\text{-}SePh)_2$ with elemental selenium have been synthesized and characterized by elemental analyses, ^1H NMR and IR spectroscopy and their crystal structures have been unequivocally determined by x-ray diffraction analyses.

Keywords: Selenium; Ligand; Mo_2Se_4 complex; Synthesis; Crystal structure

INTRODUCTION

In recent years we have been interested in studying group 6 transition metal complexes that contain various chalcogenido ligands [1–6]. Such interest stems from the importance of such complexes in biology and catalysis, as well as from their unique structures and practical uses in production of novel transition metal complexes [1–12]. In two papers published previously, we reported that reactions of the doubly bridged M_2Se_2 complexes $(\eta^5\text{-}RC_5H_4)_2M_2(CO)_2(\mu\text{-}SePh)_2$ with elemental selenium resulted in formation of a series of quadruply bridged M_2Se_4 complexes *trans/anti*- and *trans/syn*-$(\eta^5\text{-}RC_5H_4)_2M_2(\mu\text{-}Se)_2(\mu\text{-}SePh)_2$, whereas reactions of the triply bonded complexes $(\eta^5\text{-}RC_5H_4)_2M_2(CO)_4$ with dibenzyldiselenide unexpectedly afforded clusters: *trans/*

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anti- and *trans*/*syn*-(η^5-$RC_5H_4)_2M_2(\mu$-Se$)_2(\mu$-SeCH$_2$Ph$)_2$ (M = Mo, W) [5,12]. As a continuation of this work, herein we report the syntheses and crystal structures of quadruply bridged Mo_2Se_4 complexes *trans*/*anti*-(η^5-$CH_3O_2CC_5H_4)_2Mo_2(\mu$-Se$)_2$ (μ-SeCH$_2$Ph)(μ-SePh) and *trans*/*syn*-(η^5-$C_2H_5O_2CC_5H_4)_2Mo_2(\mu$-Se$)_2(\mu$-SePh$)_2$.

EXPERIMENTAL

Physical Measurements

All reactions were carried out under purified dinitrogen atmosphere using Schlenk techniques. THF and toluene were refluxed and distilled from Na/benzophenone under dinitrogen atmosphere and deoxygenated by bubbling with dinitrogen for 15 min before use. Silica gel for preparative TLC was 300–400 mesh. $(PhCH_2)_2Se_2$ [13], triply bonded dimolybdenum complex (η^5-$CH_3O_2CC_5H_4)_2Mo_2(CO)_4$ [14] and doubly bonded dimolybdenum complex (η^5-$C_2H_5O_2CC_5H_4)_2Mo_2(CO)_2(\mu$-SePh$)_2$ [1] were prepared according to the literature methods. Progress of the reactions was monitored by TLC and products were isolated by preparative TLC and further recrystallized from CH_2Cl_2 and hexane mixed solvent. NMR spectra were determined on a Bruker ARX-500 spectrometer using TMS as an external standard in $CDCl_3$. IR spectra were recorded on a Nicolet FT-5DX spectrophotometer as KBr disks in the range 400–4000 cm^{-1}. Analyses for C and H were performed on a Yanaco CHN Corder MT-3 instrument. Melting points were measured on a Yanaco MP-500 micromelting point apparatus and are uncorrected.

Syntheses of Complexes 1 and 2

A 100-cm^3 three-necked flask fitted with a magnetic stir-bar, a rubber septum and a reflux condenser topped with a nitrogen inlet tube was charged with 0.825 g (1.5 mmol) (η^5-$CH_3O_2CC_5H_4)_2Mo_2(CO)_4$ and 0.510 g (1.5 mmol) $(PhCH_2)_2Se_2$ in 40 cm^3 of toluene. The mixture was refluxed for 2 h, during which the color changed from brown-yellow to green. The solvent was removed *in vacuo*. The residue was subjected to TLC separation using CH_2Cl_2 as the eluent. The three green bands in decreasing order of R_f (0.45, 0.43 and 0.40) values afforded 0.162 g (12%) of *trans*/*anti*-(η^5-$CH_3O_2CC_5H_4)_2Mo_2(\mu$-Se$)_2(\mu$-SeCH$_2Ph)_2$ as a green solid, 0.162 g (11.7%) of *trans*/*anti*-(η^5-$CH_3O_2CC_5H_4)_2Mo_2(\mu$-Se$)_2(\mu$-SePh)($\mu$-SeCH$_2$Ph) (complex **1**) as a green solid and 0.176 g (13%) of *trans*/*syn*-(η^5-$CH_3O_2CC_5H_4)_2Mo_2(\mu$-Se$)_2(\mu$-SeCH$_2$ Ph$)_2$ as a green solid [12]. Complex **1**, m.p. 165–167°C. Anal. Calcd. for $C_{27}H_{26}Mo_2 O_4Se_4$(%): C, 35.16; H, 2.84. Found: C, 35.37; H, 2.96. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.22–6.72 (2m, 10H, 2C_6H_5); 6.68–5.80 (4m, 8H, 2C_5H_4); 3.75 (s, 6H, 2CH_3); 2.84, 2.90 (2s, 2H, CH_2). IR (KBr disk, cm^{-1}): 1724 (s, CO).

To the flask described above, 0.292 g (0.35 mmol) *trans*/*anti*- and *trans*/*syn*-(η^5-$C_2H_5O_2CC_5H_4)_2Mo_2(CO)_2(\mu$-SePh$)_2$, 0.111 g (1.4 mmol) selenium powder and 40 cm^3 of THF was added. The stirred mixture was refluxed for 1 h, during which the color changed from brown-green to blue. The solvent was evaporated to dryness under vacuum. The resulting solid was chromatographed using CH_2Cl_2/petroleum ether (4:1, v/v) as the eluent on silica-gel plates. Three bands in decreasing order of R_f values (0.82, 0.48 and 0.46) gave 0.021 g of Ph_2Se_2 as a yellow solid, 0.093 g (28%)

trans/anti-(η^5-$C_2H_5O_2CC_5H_4)_2Mo_2(\mu$-Se$)_2(\mu$-SePh$)_2$ as blue crystals and 0.144 g (44%) of *trans/syn*-(η^5-$C_2H_5O_2CC_5H_4)_2Mo_2(\mu$-Se$)_2(\mu$-SePh$)_2$ (Complex **2**) as blue-violet crystals [1,5,12].

Crystal Structure Determination

Single crystals of Complex **1** were obtained by layering a dichloromethane solution with hexane at −5°C. Single crystals of Complex **2** were obtained by slow evaporation of its dichloromethane and hexane solution at about 5°C. For each complex, a single crystal suitable for X-ray diffraction analysis was mounted on a diffractometer (for **1**, Rigaku-AFC5R; for **2**, Enraf-Nonius CAD4) equipped with a graphite monochromator and Mo Kα radiation. The structures were solved by a direct phase determination method (MULTAN 82). The final refinements were accomplished by a full-matrix least-squares method with anisotropic thermal parameters for non-hydrogen atoms. All computations were performed on a MICRO-VAX II computer using the TEXSAN program package. ORTEP plots were drawn with ORTEP-3 for Windows [15]. Details of data collection and structure refinement are summarized in Table I. Fractional atomic coordinates and isotropic thermal parameters of all non-H atoms for Complexes **1** and **2** are given in Tables II and III. Selected bond distances and angles for the above complexes are presented in Tables IV and V.

TABLE I Crystallographic data for Complexes **1** and **2**

	1	**2**
Formula	$C_{27}H_{26}Mo_2O_4Se_4$	$C_{28}H_{28}Mo_2O_4Se_4$
Formula weight	922.22	936.25
Crystal size (mm)	0.90 × 0.20 × 0.05	0.3 × 0.3 × 0.2
Crystal system	Orthorhombic	Triclinic
Space group	*P*bca	$P\bar{1}$
Unit cell dimensions		
a (Å)	17.691(6)	9.8157(6)
b (Å)	31.578(8)	13.315(1)
c (Å)	10.201(6)	13.711(1)
α (°)	90.00	112.818(5)
β (°)	90.00	110.590(5)
γ (°)	90.00	97.663(7)
V (Å^3)	5699(4)	1468.7(2)
Z	8	2
D_c (g cm^{-1})	2.150	2.117
F (000)	3520	896
T(K)	296	296
μ(MoKα) (mm^{-1})	5.951	5.774
λ (Å)	0.71073	0.71069
Diffractometer	Rigaku-AFC5R	Enraf-Nonius CAD4
Scan mode	ω–2θ	ω–2θ
2θ max (°)	50	49.9
Absorption correction	Ψ-scan	Ψ-scan
Reflections collected	5620	5165
Independent reflections [$I > 3.0\sigma(I)$]	2231	3900
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
No. of parameters refined	334	343
Final R indices	$R1$, 0.044; $wR2$, 0.052	$R1$, 0.031; $wR2$, 0.040
GoF	1.09	1.07
Largest diff. peak and hole (e Å^{-3})	0.74 and −0.67	0.73 and −0.61

TABLE II Atomic coordinates and isotropic thermal parameters (Å^2) for Complex **1**

Atom	*x*/*a*	*y*/*b*	*z*/*c*	*B*(*eq*)
Mo(1)	0.76419(7)	0.10212(4)	0.1393(1)	2.46(6)
Mo(2)	0.72974(7)	0.09626(4)	0.3906(1)	2.42(6)
Se(1)	0.72910(9)	0.03405(5)	0.2439(1)	3.02(7)
Se(2)	0.76633(9)	0.16434(5)	0.2874(1)	2.99(7)
Se(3)	0.87004(9)	0.09249(5)	0.3146(1)	2.91(7)
Se(4)	0.62501(9)	0.10540(5)	0.2152(2)	2.96(7)
O(31)	0.9073(6)	0.1884(4)	−0.010(1)	4.8(7)
O(32)	0.9748(6)	0.1278(4)	0.016(1)	5.5(7)
O(41)	0.8699(7)	0.1408(4)	0.661(1)	4.8(6)
O(42)	0.7783(7)	0.1899(4)	0.635(1)	5.6(7)
C(11)	0.9128(8)	0.0360(5)	0.310(1)	3.4(8)
C(12)	0.900(1)	0.0045(5)	0.402(2)	4(1)
C(13)	0.940(1)	−0.0329(6)	0.398(2)	5(1)
C(14)	0.992(1)	−0.0414(6)	0.305(2)	5(1)
C(15)	1.006(1)	−0.0098(6)	0.208(2)	5(1)
C(16)	0.968(1)	0.0279(6)	0.210(1)	4(1)
C(20)	0.5821(8)	0.1643(5)	0.210(1)	3.5(8)
C(21)	0.5845(9)	0.1812(4)	0.072(1)	2.9(7)
C(22)	0.537(1)	0.1649(6)	−0.023(2)	4(1)
C(23)	0.542(1)	0.1814(7)	−0.152(2)	5(1)
C(24)	0.594(1)	0.2107(6)	−0.183(2)	5(1)
C(25)	0.638(1)	0.2284(5)	−0.088(2)	4(1)
C(26)	0.634(1)	0.2135(5)	0.037(2)	4.0(9)
C(31)	0.8440(9)	0.1236(5)	−0.027(1)	3.1(8)
C(32)	0.836(1)	0.0795(5)	−0.036(1)	3.6(8)
C(33)	0.760(1)	0.0713(6)	−0.071(1)	5(1)
C(34)	0.721(1)	0.1101(7)	−0.080(1)	5(1)
C(35)	0.774(1)	0.1432(6)	−0.053(1)	3.7(8)
C(36)	0.914(1)	0.1462(6)	−0.004(1)	4(1)
C(37)	0.975(1)	0.2134(7)	0.008(2)	6(1)
C(41)	0.7471(8)	0.1181(5)	0.600(1)	2.9(8)
C(42)	0.7582(8)	0.0750(6)	0.604(1)	3.6(8)
C(43)	0.690(1)	0.0550(6)	0.575(1)	4.0(9)
C(44)	0.6356(8)	0.0881(6)	0.551(1)	3.7(8)
C(45)	0.6710(9)	0.1261(5)	0.569(1)	3.3(8)
C(46)	0.8046(9)	0.1503(6)	0.634(1)	3.3(8)
C(47)	0.830(1)	0.2222(7)	0.661(2)	8(1)

RESULTS AND DISCUSSION

Complex **1** was unexpectedly synthesized from (η^5-$CH_3O_2CC_5H_4$)$_2$$Mo_2(CO)_4$ and $(PhCH_2)_2Se_2$ in refluxing toluene. The ^{1}H NMR spectrum of Complex **1** shows two singlets at 2.84 and 2.90 ppm for the methenyl group, one singlet at 3.75 ppm for the methyl groups, four multiplets in the range of 5.80–6.68 ppm for the substituted cyclopentadienyl rings and two multiplets in the range 6.72–7.22 ppm for the two phenyl groups. In the IR spectrum of Complex **1**, the absorption band of ester carbonyls appears at 1724 cm^{-1} as a broad singlet. Because Complex **1** is only one example in which two Se atoms have two different substituents, its single-crystal X-ray analysis has been carried out. Complex **1** crystallizes in the orthorhombic space group *P*bca with one formula unit in the asymmetric unit. Its crystal structure is shown in Fig. 1. As seen from Fig. 1, the molecule of Complex **1** contains two naked Se atoms, one SePh and one $SeCH_2Ph$ ligands, quadruply bridged to two Mo atoms, each carrying one η^5-$CH_3O_2CC_5H_4$ ligand. These ligands are all trans to each other with respect to the Mo–Mo vector whereas two substituents (Ph and CH_2Ph groups) are attached

TABLE III Atomic coordinates and isotropic thermal parameters (Å^2) for Complex **2**

Atom	*x/a*	*y/b*	*z/c*	*B*(*eq*)
Mo(1)	0.40135(5)	0.23205(4)	0.06499(4)	2.62(1)
Mo(2)	0.12648(5)	0.13113(4)	−0.11545(4)	2.51(1)
Se(1)	0.27147(6)	0.33177(5)	−0.03759(5)	2.81(2)
Se(2)	0.36959(7)	0.11342(5)	−0.14667(5)	3.11(2)
Se(3)	0.25668(7)	0.02702(5)	−0.01311(5)	3.27(2)
Se(4)	0.15675(7)	0.21885(5)	0.09740(5)	2.91(2)
O(1)	0.5375(6)	0.1368(4)	0.3157(4)	5.0(2)
O(2)	0.4576(6)	0.2862(5)	0.3897(4)	5.9(2)
O(3)	−0.0126(5)	−0.1977(4)	−0.3438(4)	4.8(2)
O(4)	0.0476(6)	−0.1083(4)	−0.4395(4)	5.5(2)
C(11)	0.4197(6)	0.2084(5)	−0.2152(5)	3.1(2)
C(12)	0.3297(7)	0.1695(6)	−0.3351(5)	4.0(2)
C(13)	0.3690(8)	0.2284(6)	−0.3886(5)	4.4(2)
C(14)	0.4950(8)	0.3215(6)	−0.3287(6)	4.3(2)
C(15)	0.5834(8)	0.3595(6)	−0.2117(6)	5.1(2)
C(16)	0.5469(8)	0.3037(6)	−0.1544(5)	4.5(2)
C(21)	0.1148(7)	0.3646(5)	0.1532(5)	3.1(2)
C(22)	0.1838(8)	0.4330(6)	0.2742(6)	4.5(2)
C(23)	0.1453(10)	0.5307(6)	0.3216(7)	5.6(3)
C(24)	0.0408(10)	0.5610(6)	0.2507(8)	5.5(3)
C(25)	−0.0271(9)	0.4921(6)	0.1301(7)	5.0(3)
C(26)	0.0095(7)	0.3943(6)	0.0819(6)	4.1(2)
C(31)	0.5614(7)	0.2744(5)	0.2548(5)	3.6(2)
C(32)	0.5585(7)	0.3803(5)	0.2523(5)	4.1(2)
C(33)	0.6287(8)	0.3890(6)	0.1807(6)	5.0(2)
C(34)	0.6709(7)	0.2917(7)	0.1386(6)	4.7(2)
C(35)	0.6310(7)	0.2205(6)	0.1836(5)	4.1(2)
C(36)	0.5107(7)	0.2353(6)	0.3268(5)	4.0(2)
C(37)	0.5044(8)	0.0877(7)	0.3862(6)	4.9(3)
C(38)	0.6422(8)	0.1274(7)	0.4974(6)	5.0(3)
C(41)	−0.0410(6)	−0.0170(5)	−0.2999(5)	3.4(2)
C(42)	−0.1067(7)	−0.0166(5)	−0.2233(5)	3.6(2)
C(43)	−0.1412(6)	0.0855(5)	−0.1831(5)	3.6(2)
C(44)	−0.0981(7)	0.1500(5)	−0.2340(6)	3.9(2)
C(45)	−0.0361(6)	0.0875(5)	−0.3056(5)	3.6(2)
C(46)	0.0044(7)	−0.1105(5)	−0.3687(5)	4.1(2)
C(47)	0.0214(9)	−0.2984(6)	−0.4093(7)	6.1(3)
C(48)	−0.1159(9)	−0.3812(6)	−0.5168(7)	6.2(3)

TABLE IV Selected bond distances (Å) and angles (°) for Complex **1**

Mo(1)–Mo(2)	2.641(2)	Mo(1)–Se(1)	2.479(2)
Mo(1)–Se(2)	2.479(2)	Mo(1)–Se(3)	2.607(2)
Mo(1)–Se(4)	2.583(2)	Mo(2)–Se(1)	2.470(2)
Mo(2)–Se(2)	2.480(2)	Mo(2)–Se(3)	2.603(2)
Mo(2)–Se(4)	2.592(2)	Se(3)–C(11)	1.94(2)
Se(4)–C(20)	2.01(1)	C(20)–C(21)	1.50(2)
Se(1)–Mo(1)–Se(3)	77.50(6)	Se(1)–Mo(1)–Se(2)	115.39(7)
Se(1)–Mo(1)–Mo(2)	57.57(5)	Se(3)–Mo(1)–Se(2)	70.33(6)
Se(2)–Mo(1)–Mo(2)	57.83(5)	Se(4)–Mo(1)–Mo(2)	59.47(5)
Se(1)–Mo(2)–Se(3)	77.74(6)	Se(1)–Mo(2)–Se(4)	70.55(6)
Se(1)–Mo(2)–Mo(1)	57.91(5)	Se(3)–Mo(2)–Mo(1)	59.62(5)
Mo(1)–Se(1)–Mo(2)	64.52(6)	Mo(1)–Se(2)–Mo(2)	64.38(6)
Mo(2)–Se(3)–Mo(1)	60.92(6)	Mo(2)–Se(4)–Mo(1)	61.38(6)

TABLE V Selected bond distances (Å) and angles (°) for Complex **2**

Mo(1)–Mo(2)	2.6392(7)	Mo(1)–Se(1)	2.4505(7)
Mo(1)–Se(2)	2.5867(8)	Mo(1)–Se(3)	2.4989(8)
Mo(1)–Se(4)	2.5868(8)	Mo(2)–Se(1)	2.4509(7)
Mo(2)–Se(2)	2.5929(8)	Mo(2)–Se(3)	2.4987(7)
Mo(2)–Se(4)	2.5736(7)	Se(2)–C(11)	1.951(6)
Se(1)–Mo(1)–Se(3)	115.55(3)	Se(1)–Mo(1)–Se(2)	77.74(2)
Se(1)–Mo(1)–Mo(2)	57.43(2)	Se(3)–Mo(1)–Se(2)	70.53(2)
Se(2)–Mo(1)–Mo(2)	59.48(2)	Se(4)–Mo(1)–Mo(2)	58.99(2)
Se(1)–Mo(2)–Se(3)	115.54(3)	Se(1)–Mo(2)–Se(4)	78.55(2)
Se(1)–Mo(2)–Mo(1)	57.41(2)	Se(3)–Mo(2)–Mo(1)	58.13(2)
Mo(1)–Se(1)–Mo(2)	65.16(2)	Mo(1)–Se(2)–Mo(2)	61.26(2)
Mo(2)–Se(3)–Mo(1)	63.75(2)	Mo(2)–Se(4)–Mo(1)	61.52(2)

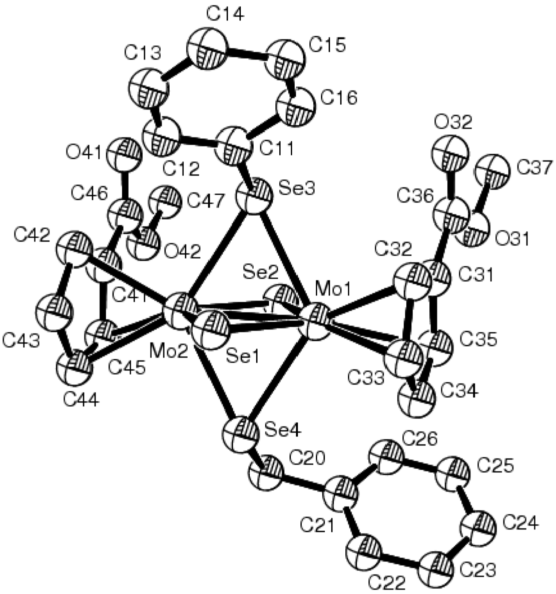

FIGURE 1 ORTEP plot of Complex **1**.

to Se atoms in the anti orientation with respect to the Mo_2Se_2 (selenolato) ring. Figure 2 is the projection of Complex **1** along a Mo=Mo vector, showing more clearly the anti orientation of the above two substituents attached to Se atoms. Furthermore, this projection indicates that the two substituted cyclopentadienyl rings are nearly eclipsed. Therefore, Complex **1** exists as a trans/anti isomer. The two Mo and two naked Se atoms, as well as the two Mo and two selenolato Se atoms comprise two planes of Mo(1)Mo(2)Se(1)Se(2) and Mo(1)Mo(2)Se(3)Se(4), which are nearly perpendicular to each other (the dihedral angle = 94.99°). The four Se atoms also form a plane, which bisects the Mo=Mo bond perpendicularly and is perpendicular to the above two planes and parallel to the two substituted cyclopentadienyl rings (the dihedral angles = 1.08 and 3.36°, respectively). Additionally, the two substituted cyclopentadienyl rings are almost parallel to each other (the dihedral angle = 2.28°). Consistent with the 18 valence-electron rule and the short Mo–Mo bond distance of 2.641(2) Å, this can

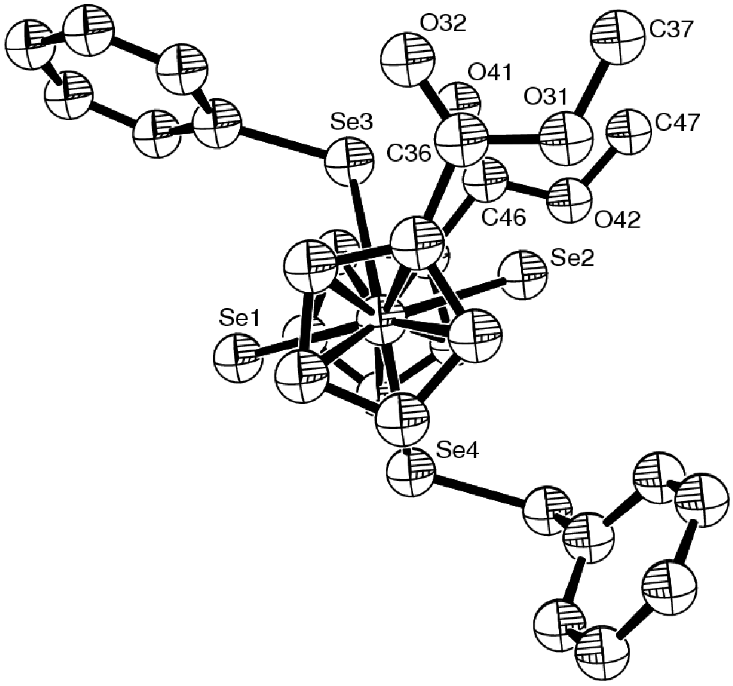

FIGURE 2 Projection of Complex **1** along Mo–Mo bond.

be assigned as a Mo=Mo double bond as described above and is comparable with that in the analogous benzylselenolato compound *trans*/*anti*-(η^5-$C_2H_5O_2CC_5H_4)_2Mo_2$ (μ-Se$)_2$(μ-SeCH$_2$Ph$)_2$ [2.6484(7) Å] and that in the ethylselenolato compound *trans*/*anti*-[(η^5-$C_5H_5)_2Mo_2$(μ-Se$)_2$(μ-SeCH$_2$CH$_3)_2$] [2.6399(6) Å] [12,16]. The non-bonding distances between the bridged atoms are 3.185 [Se(1)···Se(3)], 2.925 [Se(1)···Se(4)], 2.931 [Se(2)···Se(3)] and 3.203 Å [Se(2)···Se(4)]. These distances fall between the sum of the van der Waals radii of the two Se atoms (3.8 Å) and that of the covalent radii of the two Se atoms (2.44 Å), which indicates that there is a significant non-bonding interaction between the bridging atoms in the molecule of Complex **1** [17]. It is noted that if the bonding criterion proposed by CSD is used (*i.e.*, a bonded connection is established if the distance (*d*) between two elements A and B is in the range between Rcov(A) + Rcov(B) − t and Rcov(A) + Rcov(B) + t, where the tolerance (t) is usually set to 0.4 Å; the tolerance and Rcov (covalent radii) values can be altered by CSD Editors to force bonds in certain situations), the bridged atoms [Se(1)···Se(4) and Se(2)···Se(3)] may be assigned a bonding interaction [17]. The Mo–Se bond distances differ markedly because of the different coordination numbers of selenium. In the case of the selenido bridge, the values are 2.479(2) [Mo(1)–Se(1)], 2.479(2) [Mo(1)–Se(2)], 2.470(2) [Mo(2)–Se(1)] and 2.480(2) Å [Mo(2)–Se(2)]. In contrast, the bond distances Mo–SePh and Mo–SeCH$_2$Ph are 2.607(2) [Mo(1)–Se(3)], 2.603(2) [Mo(2)–Se(3)] and 2.583(2) [Mo(1)–Se(4)], 2.592(2) Å [Mo(2)–Se(4)]. The same bonding mode is found in the other structurally characterized complexes mentioned in this paper [12,16,18]. The Se–Ph and Se–CH$_2$Ph bond distances, 1.94(2) and 2.01(1) Å, are very close to those in the compound *trans*/*syn*-(η^5-$C_5H_5)_2Mo_2$(μ-Se$)_2$(μ-SePh$)_2$ [mean 1.941(10) Å] and that in the compound *trans*/*anti*-(η^5-$C_2H_5O_2CC_5H_4)_2Mo_2$(μ-Se$)_2$(μ-SeCH$_2$Ph$)_2$

[1.999(4) Å] [12,18]. The average Mo–Se(naked)–Mo and Mo–Se(selenolato)–Mo bond angles are 64.45(6) and 61.15(6)°, which correspond to those in *trans/anti*-(η^5-$C_5H_5)_2Mo_2(\mu$-$Se)_2(\mu$-$SeCH_2CH_3)_2$ [64.234(13) and 61.329(12)°] and *trans/anti*-(η^5-$C_2H_5O_2CC_5H_4)_2Mo_2(\mu$-$Se)_2(\mu$-$SeCH_2Ph)_2$ [64.626(17) and 61.412(17)°] [12,16].

Reactions of doubly bridged (η^5-$RC_5H_4)_2M_2(CO)_2(\mu$-$SePh)_2$ (M = Mo, W) with selenium powder produced a series of quadruply bridged M_2Se_4 complexes: *trans/anti*- and *trans/syn*-(η^5-$RC_5H_4)_2M_2(\mu$-$Se)_2(\mu$-$SePh)_2$ (M = Mo, W) [5]. These compounds were well characterized by elemental analyses, ^{1}H NMR, ^{13}C NMR, ^{77}Se NMR and IR spectroscopies. Recently X-ray-quality single crystals of one of the reported quadruply bridged complexes (Complex **2** (η^5-$C_2H_5O_2CC_5H_4)_2Mo_2(\mu$-$Se)_2(\mu$-$SePh)_2$) have been obtained and its crystal structure has been determined by X-ray diffraction analysis. Complex **2** belongs to the triclinic space group $P\bar{1}$. Although the crystal structure of the parent quadruply bridged complex *trans/syn*-(η^5-$C_5H_5)_2$-$Mo_2(\mu$-$Se)_2(\mu$-$SePh)_2$ prepared by another route is known, that of complex **2** is the first reported example of a complex containing substituted cyclopentadienyl and aryl selenolato ligands [18]. As seen from Fig. 3, the X-ray diffraction analysis reveals that Complex **2** consists of two η^5-$C_2H_5O_2CC_5H_4Mo$ fragments bridged by two phenyl selenolato groups and two selenium atoms. Although, geometrically, the Mo_2Se_4 core of Complex **2** is the same as that of Complex **1**, the two phenyl groups attached to Se atoms are in a syn position with respect to the Mo(1)Mo(2)Se(2)Se(4) plane. Figure 4 is the projection of Complex **2** along a Mo=Mo vector. Also more clearly seen from Fig. 4, the two phenyl groups attached to Se atoms are syn to each other. In addition, this projection indicates that the two substituted cyclopentadienyl rings are staggered. Therefore, this molecule exists as a trans/syn isomer. The Mo=Mo double bond distance is 2.6592(7) Å, which is slightly greater than that of Complex **1** and very close to that of *trans/syn*-(η^5-$C_5H_5)_2Mo_2(\mu$-$Se)_2(\mu$-$SePh)_2$

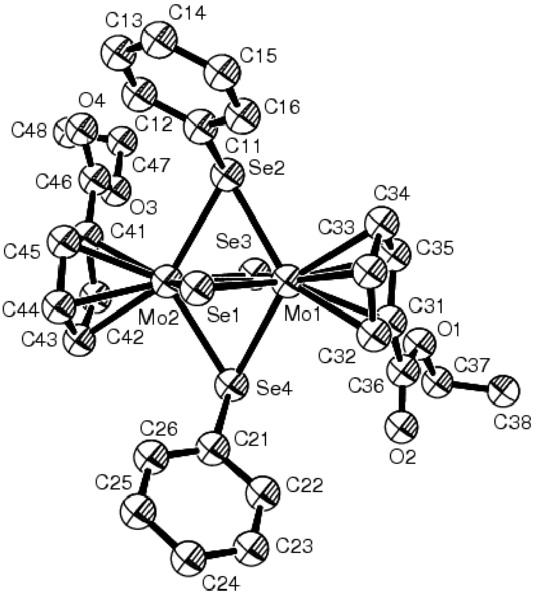

FIGURE 3 ORTEP plot of Complex **2**.

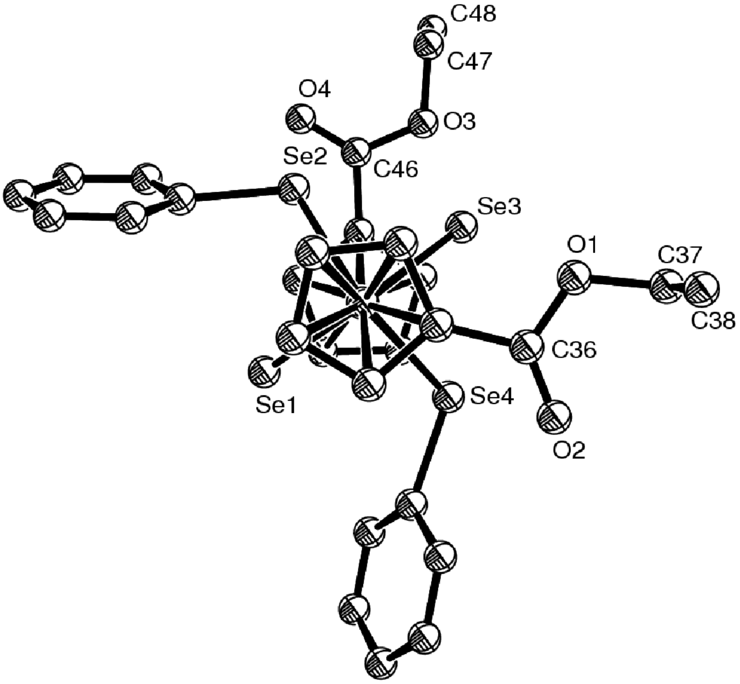

FIGURE 4 Projection of Complex **2** along Mo–Mo bond.

[2.653(2) Å]. Short contacts between the bridging Se atoms are observed: 3.163 [Se(1)···Se(2)], 3.182 [Se(1)···Se(4)], 2.937 [Se(2)···Se(3)] and 2.914 Å [Se(3)···Se(4)]. These values are between the sum of the van der Waals radii of the two Se atoms (3.8 Å) and that of the covalent radii of the two Se atoms (2.44 Å), indicating there is a marked non-bonding interaction between the bridging atoms in Complex **2** [17]. As described above, if the CSD criterion is used, the bridged atoms [Se(2)···Se(3) and Se(3)···Se(4)] may be assigned as bonding interactions [17]. The average Mo–Se(naked) bond distances Mo–Se(1) and Mo–Se(3) are 2.4507(7) and 2.4988(8) Å whereas those in *trans/syn*-[(η^5-C_5H_5)$_2$$Mo_2$($\mu$-Se)$_2$($\mu$-SePh)$_2$] are 2.463(2) and 2.505(2) Å, showing that the Mo–Se(syn to the phenyl groups) bond distance is shorter than that of Mo-Se(anti to the phenyl groups) by *ca.* 0.04 Å. The average Mo–Se(selenolato) bond distance is 2.5850(8) Å and close to that in *trans/syn*-(η^5-C_5H_5)$_2$$Mo_2$($\mu$-Se)$_2$($\mu$-SePh)$_2$ [2.599(2) Å]. The bond angles Mo(1)–Se(1)–Mo(2) and Mo(1)–Se(3)–Mo(2) are 65.16(2) and 63.75(2)° whereas the bond angles Mo(1)–Se(2)–Mo(2) and Mo(1)–Se(2)–Mo(2) are 61.26(2) and 61.52(2)°. A similar mode is also found in *trans/syn*-[(η^5-C_5H_5)$_2$$Mo_2$($\mu$-Se)$_2$($\mu$-SePh)$_2$] [18].

Acknowledgment

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Supplementary Data

Full crystallographic data (CCDC 218954 for Complex **1** and CCDC 154333 for Complex **2**) have been deposited at the Cambridge Crystallographic Data Centre and are available on request from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http//www.ccdc.cam.ac.uk).

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