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Contribution from the Departments of Chemistry, University of Calgary,
Calgary, Alberta, Canada T2N 1N4, and University of Manchester, Manchester M13 9PL, England

Synthesis and X-ray Structure Determination of $[PPh_4]_2[Cl_3W\{\mu\text{-}Se(Cl)\}(\mu\text{-}SePh)_2WCl_3]\cdot 2CH_2Cl_2$: Single-Crystal ESR Study of a Mixed-Oxidation-State Binuclear Tungsten(III)–Tungsten(IV) Complex Dispersed in a Diamagnetic Crystal Matrix

Joanne M. Ball,[1a] P. Michael Boorman,*[,1a] James F. Fait,[1a] Heinz-Bernhard Kraatz,[1a]
John F. Richardson,[1a] David Collison,[1b] and Frank E. Mabbs*[,1b]

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Reaction of $WCl_4(Me_2S)_2$ with $Me_3SiSePh$ in CH_2Cl_2 solution, followed by addition of PPh_4Cl, yields a mixture of the two compounds $[PPh_4]_2[Cl_3W(\mu\text{-}Se)(\mu\text{-}SePh)_2WCl_3]\cdot 2CH_2Cl_2$ (**1**) and its mixed-oxidation-state analogue, $[PPh_4]_2[Cl_3W(\mu\text{-}Cl)(\mu\text{-}SePh)_2WCl_3]\cdot 2CH_2Cl_2$ (**2**). The compounds are isostructural and isomorphous and in some preparations cocrystallize. Crystals of a sample containing primarily **1** were subjected to an X-ray structure determination. Crystal data: monoclinic, space group, $C2/c$, $a = 22.838$ (3) Å, $b = 12.208$ (2) Å, $c = 24.313$ (5) Å, $\beta = 104.64$ (1)°, $V = 6558.8$ Å^3, $Z = 4$, $R = 0.051$ ($R_w = 0.046$) for 357 parameters and 3742 unique observed reflections. The geometry of the anion of **1** is confacial bioctahedral, with three Se atoms in the bridging positions. The W–W bond length is 2.5641 (8) Å, consistent with the presence of a formal double bond between the two d^2 metal centers. ^{77}Se NMR studies showed two resonances, consistent with this structure being retained in solution. An ESR study of the powdered crystals of one sample indicated the presence of a paramagnetic impurity, identified as the anion of **2**. This enabled us to carry out a single-crystal ESR study of this anion in a diamagnetic matrix of complex **1**. There is a very large anisotropy in the crystal g values, with one (that close to the W–W vector) being considerably greater than 2. Hyperfine interactions with ^{183}W and ^{35,37}Cl are observed in some orientations, a fact which is used to assign a ground-state electronic configuration to the ion.

Introduction

In an earlier paper,[2] we described the preparation, crystal structure, and electron spin resonance spectral properties of the mixed oxidation state, W(III)–W(IV), complex $[AsPh_4]_2[Cl_3W(\mu\text{-}Cl)(\mu\text{-}SPh)_2WCl_3]\cdot 1.4CH_2Cl_2$ (**3**). The ESR spectra of the powdered solid (77 and 298 K) and of a frozen solution in CH_2Cl_2 (77 K) were obtained. They were interpreted as a rhombic, $S = {}^1/_2$ system, and simulated on this basis. The spectra were characterized by a large anisotropy in the g values, with one g value being considerably greater than 2. It was presumed that this value was associated with the W–W direction, but we were unable to obtain sufficiently large crystals to carry out single-crystal ESR studies to verify this. The interpretation was shown to be qualitatively compatible with the theoretical treatment of confacial bioctahedral complexes by Summerville and Hoffmann.[3] For the C_{2v} symmetry of the complex, the possible ground-state configuration would be $(1A_1)^2(1B_1)^2(2A_1)^1$ or $(1A_1)^2(2A_1)^2(1B_1)^1$, depending on the ordering of the $2A_1$ and $1B_1$ energy levels, which are derived from the e′ pair in D_{3h} symmetry.[2,3] By preparation of the selenium analogue of **3**, it was anticipated that additional information might be obtained from hyperfine coupling with ^{77}Se, and the system would enable us to diversify our attempts to grow crystals of adequate size to obtain single-crystal ESR data. In this paper, we present the results of this study, which focuses on the crystal structure and single-crystal ESR spectral properties of the compound $[PPh_4]_2[Cl_3W(\mu\text{-}SePh)_2\{\mu\text{-}Se(Cl)\}WCl_3]\cdot 2CH_2Cl_2$. Quite fortuitously, this system provided us with an ideal situation for an ESR study, namely a diamagnetic matrix in which a paramagnetic "impurity" is dispersed, and crystals of sufficient size and quality to study the directional dependence of the ESR parameters.

Experimental Section

General Procedures. All manipulations were carried out in a dry, N_2-filled glovebox, or on a standard double manifold. Analytical grade solvents were dried (CH_2Cl_2 over P_4O_{10} and then CaH_2; hexanes over CaH_2) and freshly distilled under an atmosphere of dry nitrogen immediately before use. The compound $WCl_4(Me_2S)_2$ was prepared as previously described.[4] (Phenylseleno)trimethylsilane was prepared from Me_3SiCl and Na^+PhSe^- in refluxing THF solution.[5] The sodium salt was previously generated in situ by reduction of diphenyl diselenide with sodium in liquid ammonia. The $Me_3SiSePh$ was purified by distillation at 5 Torr of pressure, at which it boiled between 90 and 92 °C. Its purity was checked via its ^{1}H and ^{77}Se NMR spectra. PPh_4Cl (Aldrich Chemicals) was dried at 100 °C under vacuum for 12 h before use.

Synthesis. The compound $[PPh_4]_2[Cl_3W(\mu\text{-}SePh)_2\{\mu\text{-}Se(Cl)\}WCl_3]\cdot 2CH_2Cl_2$ was prepared in a two-step process from $WCl_4(Me_2S)_2$. To a stirred solution of $WCl_4(Me_2S)_2$ (2.98 g, 6.65 mmol) in CH_2Cl_2 (ca. 30 mmol) was added a solution of $Me_3SiSePh$ (1.524 g, 6.65 mmol) in the same solvent (ca. 18 mL). After the mixture was stirred overnight, tetraphenylphosphonium chloride (2.49 g, 6.65 mmol) was added and the stirring was continued for a further 24 h. After filtration, hexanes were added (ca. 5 mL) and the solution was cooled to 5 °C whereupon the product slowly crystallized out. Anal. Calcd for $[PPh_4]_2[Cl_3W(\mu\text{-}SePh)WCl_3]\cdot 2CH_2Cl_2$: C, 40.91; H, 2.99. Found: C, 40.77; H, 2.94. IR data (2000–250 cm^{-1}, KBr disk): 280 (sh), 290 (m), 320 (m) (all ν(W–Cl)); 527 (vs); 690 (vs); 723 (vs); 758 (m), 955 (m), 995 (m); 1026 (m); 1108 (vs); 1164 (w); 1186 (w), 1436 (vs); 1483 (s); 1585 (m). UV–vis data (CH_2Cl_2 solution; λ_{max}, nm (ϵ)): 390 (6750), 431 (6615); 570 (685).

^{1}H NMR (δ): $P(C_6H_5)_4^+$, 7.85–7.48, m, (40); $Se(C_6H_5)$, 7.26–7.19; pseudotriplet; 6.94–6.84, m, (total = 10).

^{13}C NMR (δ): $P(C_6H_5)_4^+$, 136.20, 136.14 (d), ipso C; 135.06, 134.86 (d), ortho C; 131.29, 131.04 (d), meta C; 117.16, para C; $Se(C_6H_5)$, 132.99, ipso C; 128.12, ortho C; 127.96, meta C; 118.94, para C.

In subsequent preparations with slightly different concentrations or reaction times, the product contained a greater proportion of the μ-Cl anion rather than the μ-Se analogue on which the first crystal structure and the single-crystal ESR studies were performed. No systematic correlation between conditions and the product mix could be identified, but when the crude product was first recrystallized from acetonitrile, followed by dichloromethane, only the seleno-bridged anion of **1** was detected, both spectroscopically and crystallographically. A pure sample of the complex **2** was not successfully prepared.

X-ray Crystal Structure of $[PPh_4]_2[Cl_3W(\mu\text{-}SePh)_2(\mu\text{-}Se)WCl_3]\cdot 2CH_2Cl_2$. Two complete crystal structure determinations were carried out, the first on a crystal from the batch used in the ESR study and the second from a sample initially recrystallized from acetonitrile, followed by dichloromethane. Only the second of these (by J.F.F.) is reported in this paper, but results from the first (by J.F.R.) show no substantial differences from those described here. The duplicate analysis was prompted by the possibility that the second preparation was essentially

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(1) (a) University of Calgary. (b) University of Manchester.

(2) Ball, J. M.; Boorman, P. M.; Moynihan, K. J.; Patel, V. D.; Richardson, J. F.; Collison, D.; Mabbs, F. E. *J. Chem. Soc., Dalton Trans.* **1983**, 2479.

(3) Summerville, R. H.; Hoffmann, R. *J. Am. Chem. Soc.* **1979**, *101*, 3821.

(4) (a) Boorman, P. M.; Chivers, T.; Mahadev, K. N. *Can. J. Chem.* **1975**, *53*, 383. (b) Schaefer-King, M. A.; McCarley, R. E. *Inorg. Chem.* **1973**, *12*, 1972.

(5) Miyoshi, N.; Ishii, H.; Kondo, K.; Murai, S.; Sonoda, N. *Synthesis* **1979**, *4*, 300.

0020-1669/90/1329-3290$02.50/0

Table I. Crystallographic Data for $W_2Se_3Cl_6C_{12}H_{10}[2P(C_6H_5)_4]\cdot 2CH_2Cl_2$

$W_2Se_3Cl_6C_{12}H_{10}[2P(C_6H_5)_4]\cdot 2CH_2Cl_2$	fw = 1820.17
$a = 22.838$ (3) Å	space group: $C2/c$
$b = 12.208$ (2) Å	$T = 25$ °C
$c = 24.313$ (5) Å	$\lambda = 0.71069$ Å
$\beta = 104.64$ (1)°	$\mu = 56.74$ cm^{-1}
$V = 6558.76$ Å^3	abs cor F_oA: $0.505 < A < 1.273$
$Z = 4$	$R = 0.051$
$D_c = 1.843$ g cm^{-3}	$R_w = 0.046$

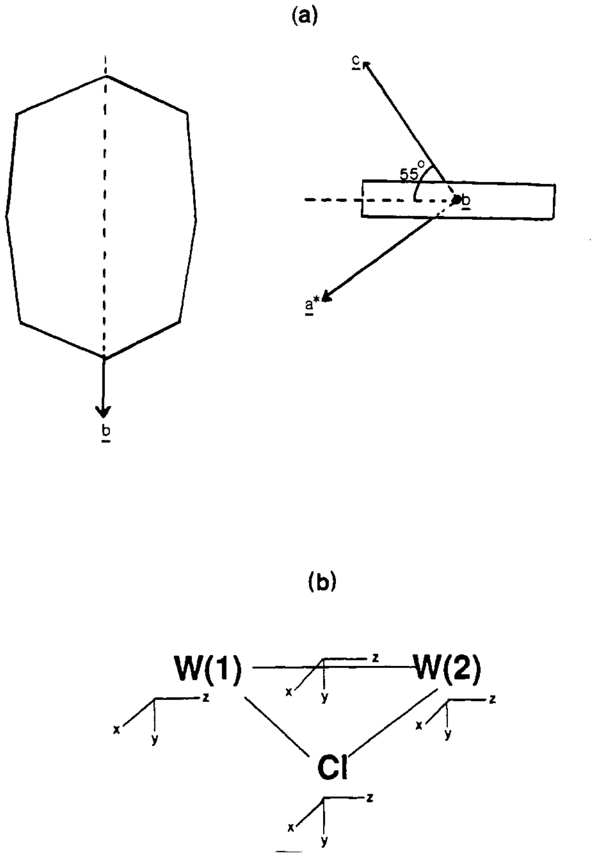

Figure 1. (a) Morphology and crystal axes of the crystal(s) used for ESR measurements. (b) Molecular axes and directions of principal molecular g values.

pure compound **1** and would not be subject to any minor disorder as a result of the presence of small amounts of compound **2**. In addition, we were able to obtain data to a much larger value of 2θ from this crystal.

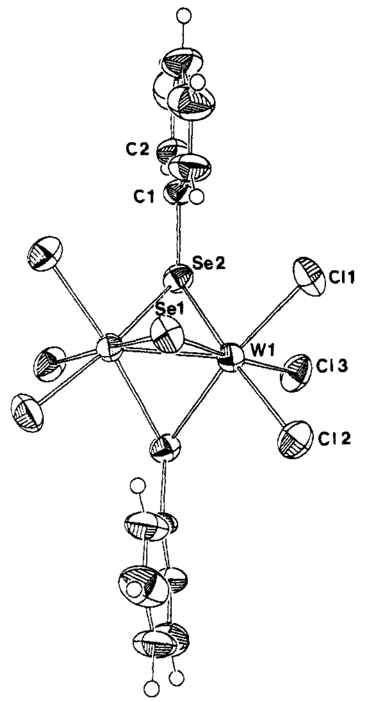

Figure 2. ORTEP plot of the anion $[Cl_3W(\mu\text{-}SePh)_2(\mu\text{-}Se)WCl_3]^{2-}$ showing the atom-labeling scheme (50% probability ellipsoids for non-hydrogen atoms).

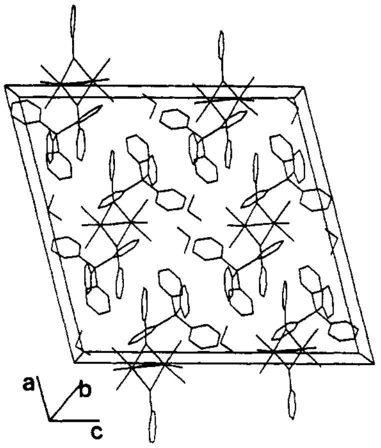

Figure 3. View of the unit cell contents of **1** (**2**) showing the orientation of the anions with respect to the crystal axes.

A suitable transparent, dark red, block-shaped crystal of approximate dimensions 0.2 × 0.3 × 0.4 mm^3 was wedged in a Lindemann glass capillary and mounted on an Enraf-Nonius CAD4 diffractometer. Unit cell parameters and their standard deviations were derived from the setting angles of 25 reflections in the range $10.48 < \theta < 15.53°$. Reduced cell calculations did not indicate any higher metric symmetry. Crystal and instrumental instability were monitored through the measurement of three standard reflections every 1 h of exposure time. There was no indication of any decomposition. Data were collected in the ω–2θ scan mode, and corrected for reflection width, scale variation, and Lorentz and polarization effects. The pertinent crystallographic data are collected in Table I. The structure was solved by using SIMPEL;[6] the remaining non-hydrogen atoms were located in a series of difference Fourier maps after refining the scale and thermal parameters. The data were corrected for absorption by using DIFABS[7] after isotropic refinement. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed in calculated positions with fixed isotropic temperature factors, which were not refined. The model converged at $R = 0.051$. The final values of the refined positional parameters are presented in Table II. All other supporting data are available as supplementary material. Neutral-atom scattering factors were used, with anomalous dispersion corrections applied.[8] No corrections for extinction were made. All calculations were carried out on a Zenith 386 running UNIX, version 3, at the University of Calgary with the program package XTAL.[9]

^{77}Se NMR Studies. All ^{77}Se NMR spectra were recorded on a Bruker AM 400 spectrometer, equipped with an Aspect 3000 data system, using a D_2O lock. Spectra were referenced, by sample exchange, to neat Me_2Se at 0 ppm. The spectrum of **1** was obtained from a saturated solution in CH_2Cl_2 (ca. 0.05 g/4 mL solvent), contained in a 10-mm-o.d. NMR tube with the lock substance contained in a 4-mm-o.d. insert. Typical ^{77}Se NMR spectra were recorded by using a 90° pulse with a 20-μs pulse width, a delay of 0.082 s, and an acquisition time of 0.2 s, at operating frequencies of 76.31 and 76.39 MHz.

ESR Studies. The single-crystal studies were carried out on small (ca. 1 × 1 × 0.5 mm), oriented (by standard X-ray techniques) single crystals at X-band frequencies and a temperature of 77 K. The spectrometer used was a Varian E-112 with low temperatures obtained by using an Oxford

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(6) Schenk, H.; Hall, S. R. SIMPEL. *XTAL2.4 User's Manual*; Hall, S. R.; Stewart, J. M., Eds.; Universities of Western Australia and Maryland: Nedlands, Australia, and College Park, MD.

(7) Program DIFABS, Walker, N.; Stewart, D. *Acta Crystallogr.* **1983**, *A39*, 158.

(8) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

(9) Hall, S. R.; Stewart, J. M., Eds. *XTAL2.4 User's Manual*; Universities of Western Australia and Maryland: Nedlands, Australia, and College Park, MD.

Table II. Non-Hydrogen Atom Coordinates

atom	*x*	*y*	*z*	1000*U*
W(1)	0.50545 (2)	0.73627 (3)	0.30379 (2)	37.5
Se(1)	0.50000	0.5684 (1)	0.25000	50.3
Se(2)	0.41697 (5)	0.83435 (9)	0.23694 (5)	42.4
P(1)	0.6689 (1)	0.2458 (2)	0.3751 (1)	39.4
Cl(1)	0.4378 (1)	0.6566 (3)	0.3557 (1)	62.3
Cl(2)	0.5891 (1)	0.6690 (2)	0.3770 (1)	56.1
Cl(3)	0.5060 (1)	0.8992 (1)	0.3623 (1)	55.4
C(1)	0.3400 (4)	0.760 (1)	0.2212 (4)	46.8
C(2)	0.2898 (5)	0.823 (1)	0.2031 (5)	59.7
C(3)	0.2332 (7)	0.785 (2)	0.1907 (6)	92.3
C(4)	0.2260 (6)	0.675 (2)	0.1991 (7)	89.9
C(5)	0.2750 (7)	0.604 (1)	0.2184 (7)	87.1
C(6)	0.3315 (6)	0.649 (1)	0.2300 (6)	67.1
C(11)	0.7337 (5)	0.3328 (8)	0.3821 (4)	41.0
C(12)	0.7445 (6)	0.417 (1)	0.4205 (5)	56.2
C(13)	0.7972 (7)	0.481 (1)	0.4268 (6)	74.5
C(14)	0.8384 (6)	0.457 (1)	0.3979 (5)	60.1
C(15)	0.8270 (5)	0.373 (1)	0.3583 (5)	58.1
C(16)	0.7742 (5)	0.3109 (9)	0.3498 (4)	48.6
C(21)	0.6270 (4)	0.2464 (9)	0.3019 (4)	45.2
C(22)	0.5998 (5)	0.1515 (9)	0.2757 (5)	50.7
C(23)	0.5656 (6)	0.156 (1)	0.2200 (5)	67.8
C(24)	0.5598 (5)	0.253 (1)	0.1911 (4)	59.1
C(25)	0.5871 (6)	0.346 (1)	0.2164 (5)	62.2
C(26)	0.6204 (5)	0.3445 (9)	0.2724 (5)	51.5
C(31)	0.6232 (5)	0.2991 (8)	0.4197 (4)	39.7
C(32)	0.6327 (5)	0.262 (1)	0.4752 (5)	56.0
C(33)	0.6016 (6)	0.306 (1)	0.5105(5)	67.1
C(34)	0.5617 (6)	0.390 (1)	0.4906 (5)	66.5
C(35)	0.5512 (6)	0.425 (1)	0.4356 (6)	80.0
C(36)	0.5828 (6)	0.380 (1)	0.4001 (5)	57.2
C(41)	0.6928 (5)	0.1097 (8)	0.3988 (4)	39.2
C(42)	0.6504 (5)	0.029 (1)	0.4016 (5)	52.7
C(43)	0.6684 (7)	−0.0736 (9)	0.4208 (5)	64.1
C(44)	0.7288 (7)	−0.098 (1)	0.4357 (6)	71.3
C(45)	0.7714 (6)	−0.024 (1)	0.4332 (6)	72.7
C(46)	0.7535 (6)	0.0832 (9)	0.4144 (6)	63.5
Cl(4)	0.5132 (2)	0.1181 (3)	0.0455 (2)	100.2
Cl(5)	0.6109 (3)	0.2628 (5)	0.0427 (2)	156.1
C(7)	0.5503 (7)	0.192 (2)	0.0048 (6)	115.6

Table III. Selected Bond Length and Bond Angle Data for the Anion for **I**

	Bond Lengths (Å)		
W(1)–W(1)′	2.5641 (8)	Cl(2)–W(1)	2.403 (3)
Se(1)–W(1)	2.417 (1)	Cl(3)–W(1)	2.444 (3)
Se(2)–W(1)	2.549 (1)	C(1)–Se(2)	1.93 (1)
Se(2)–W(1)′	2.538 (1)	C(1)–C(2)	1.35 (2)
Cl(1)–W(1)	2.431 (4)		
	Bond Angles (deg)		
Se(1)–W(1)–Se(2)	97.42 (3)	Se(2)–W(1)–Cl(3)	82.87 (7)
Se(1)–W(1)–Cl(1)	89.37 (8)	Se(2)–W(1)–W(1)′	59.52 (3)
Se(1)–W(1)–Cl(2)	91.92 (7)	Se(2)–W(1)–Se(2)	92.79 (4)
Se(1)–W(1)–Cl(3)	175.59 (8)	W(1)–W(1)′–Se(2)	59.95 (3)
Se(1)–W(1)–W(1)′	57.97 (2)	W(1)–Se(1)–W(1)′	64.06 (4)
Se(1)–W(1)–Se(2)	97.72 (3)	W(1)–Se(2)–C(1)	116.2 (3)
Se(2)–W(1)–Cl(1)	90.77 (8)	W(1)–Se(2)–W(1)′	60.54 (3)
Se(2)–W(1)–Cl(2)	170.60 (8)		

Instruments ESR 9 continuous-flow cryostat coupled to a Harwell DT temperature controller. Because of the small size of the crystals, their morphology (see Figure 1a) and the orientation of the binuclear anions in the unit cell (Figure 3) we collected the ESR spectra with the magnetic field parallel to the crystal *b* axis and at 10° intervals in the *ac* plane. Proper alignment of the crystals was ensured by the observation of ESR spectra due to a single magnetic site in these orientations, as required by the crystallography.

Results and Discussion

Synthetic Reactions. By comparison with the reaction of Me_3SiSPh with $WCl_4(Me_2S)_2$, followed by addition of PPh_4Cl, (see ref 2), it was anticipated that the analogous reaction with the (phenylseleno)trimethylsilane would yield pure samples of the mixed-oxidation-state selenolato complex **2**. Instead, the product is analogous to those obtained from reactions using (*alkyl*thio)-trimethylsilane, rather than *arene*thiolates.[10] These yield $[Cl_3W(\mu\text{-}SR)_2(\mu\text{-}S)WCl_3]^{2-}$ (W(IV)–W(IV)) as opposed to $[Cl_3W(\mu\text{-}SAr)_2(\mu\text{-}Cl)WCl_3]^{2-}$ (W(III)–W(IV)) salts. The cleavage of alkyl–sulfur bonds in synthetic reactions using Me_3SiSR is a frequent occurrence, but the thermodynamically more stable aryl–S bond is seldom broken under the conditions of this type of reaction. Rather, degradation of the intermediate thiolato–metal complexes is likely to occur via reductive elimination of ArSSAr. This mechanism was suggested for the reduction of tungsten during the formation of **3**.[2] There is virtually no information available in the literature on the use of $Me_3SiSePh$, and hence the observation of a dearylation reaction in the synthesis of **1** seems to be new. However, the C–Se bond has been shown to be weaker than the C–S bond in both diaryl and dialkyl chalcogenides, so this result may not be unexpected.[11] Attempts to identify the selenium-containing byproducts via ^{77}Se NMR have been made. There are several ^{77}Se resonances (notably at ca. 160, 482, and ca. 600 ppm) in the spectrum of the reaction solution, and assignments are uncertain, but one product is tentatively identified as Ph_2Se_2 (δ 482, referenced to Me_2Se at 0 ppm). Resonances at +1000 and +923 ppm were identified as belonging to the product, compound **1**, by directly measuring the spectrum of this species. From the intensity ratio of approximately 1:2, they are assigned to the μ-Se and the μ-SePh groups, respectively. Although the resonance assigned to the μ-Se is at a chemical shift very similar to examples reported by Ibers and co-workers,[12] the μ-SePh resonance is at much lower field than has been reported[13] for d^{10} metal systems such as Hg(II) and Cd(II). This is perhaps related to the markedly different bond angles and the presence of metal–metal bonding in **1**. (See discussion of structure, below.) The silyl reagent $Me_3SiSePh$ gives a ^{77}Se resonance at 100 ppm, and this is totally absent in the spectrum of the reaction solution, indicating that the reagent is completely converted to Me_3SiCl.

The X-ray crystal structure of the product obtained from the reaction of $Me_3SiSePh$, $WCl_4(Me_2S)_2$, and PPh_4Cl, and recrystallized from CH_3CN and then CH_2Cl_2, confirmed that its identity is $[PPh_4]_2[Cl_3W(\mu\text{-}SePh)_2(\mu\text{-}Se)WCl_3]\cdot 2CH_2Cl_2$ (**1**) (Figure 2). The two tungsten atoms have identical environments, imposed by a 2-fold axis that passes through the μ-Se(1) atom. The anion of **1** would be expected to be diamagnetic, since it contains two d^2, W(IV) centers strongly coupled via a W=W bond. The bond length, 2.5641 (8) Å (Table III) is longer than that of the anion of **3**, 2.519 (2) Å. The additional d electron in the W(III)/W(IV) mixed-oxidation-state complex enables it to achieve a formal metal–metal bond order of 2.5; hence, this shortening is predicted.[3] The angles subtended at the bridging atoms, W–Se–W, are considerably smaller than the 70.5° predicted by Cotton and Ucko[14] for a "pure" confacial bioctahedral structure, i.e., one with no metal–metal bond. The bond lengths to the μ-Se ion are shorter (2.417 (1) Å) than those between W and the μ-Se(Ph) atoms (2.549 (1) and 2.538 (1) Å) as expected by comparison with thiolate/sulfide chemistry.[10] An earlier structure determination on a crystal obtained from CH_2Cl_2 solution without prior recrystallization from MeCN gave essentially the same structural parameters, even though this sample had different ESR properties. This suggests that the concentration of the cocrystallized compound **2** in the lattice of **1** is not within the detection limits of the X-ray experiment.

Electron Spin Resonance Studies. Prior to obtaining the X-ray crystal structure of **1**, we made a routine study of the ESR properties of the compound, both as a powder and as a frozen

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(10) Boorman, P. M.; Ball, J. M.; Moynihan, K. J.; Patel, V. D.; Richardson, J. F. *Can. J. Chem.* **1983**, *61*, 2809.

(11) Batt, L. In *The Chemistry of Organic Selenium and Tellurium Compounds*; Patai, S.; Rappoport, Z., Eds.; John Wiley: London and New York, 1986.

(12) Wardle, R. W. M.; Bhaduri, S.; Chau, C.-N.; Ibers, J. A. *Inorg. Chem.* **1988**, *27*, 1747.

(13) (a) Dean, P. A. W.; Vittal, J. J.; Payne, N. C. *Inorg. Chem.* **1987**, *26*, 1683. (b) Dean, P. A. W.; Vittal, J. J. *Inorg. Chem.* **1987**, *26*, 278.

(14) Cotton, F. A.; Ucko, D. *Inorg. Chim. Acta* **1972**, *6*, 161.

Table IV. ESR Parameters for **2** and **3**

ESR param	compd **2**[e]	compd **3**[a]
$g_1(\equiv g_{cc} = g_{zz})$	2.317[b]	2.343
$g_2(\equiv g_{a^*a^*} = g_{xx})$	1.901[b]	1.896
$g_3(\equiv g_{bb} = g_{yy})$	1.777[b]	1.752
$A_{zz}(^{183}W)/mT$	2.6	
$A_{xx}(^{183}W)/mT$	*c*	
$A_{yy}(^{183}W)/mT$	3.4	
$a_{zz}(^{35,37}Cl)/mT$	~0.3[d]	
$a_{xx}(^{35,37}Cl)/mT$	1.1	
$a_{yy}(^{35,37}Cl)/mT$	~0.4	

[a] From ref. 2. [b] Average values from two different crystals. Estimated error ±0.001. [c] Not resolved. [d] Estimated from the peak–peak line width for the resonance due to tungsten isotopes with $I = 0$. [e] The *g* values and hyperfine splittings were measured directly from the observed spectra.

solution, and discovered that its behavior was remarkably similar to that of the thiolato complex **3**. It was therefore anticipated that it would contain the mixed-oxidation-state anion $[Cl_3W(\mu\text{-}SePh)_2(\mu\text{-}Cl)WCl_3]^{2-}$, rather than the diamagnetic bis (tungsten(IV)) anion of **1**. Hence, when the first X-ray structure showed that the crystal contained μ-Se, rather than μ-Cl, it was deduced that this specific sample of the reaction product must be primarily **1**, with small quantities of the anion of **2** dispersed in the lattice. In view of the fact that the thiolato complex **3** is isomorphous with **1**, this supposition seemed justified.

The ESR spectra at most orientations studied are as expected for a one-unpaired electron dimer consisting of equivalent tungsten atoms (^{183}W, 14.3%, $I = {}^1/_2$). In addition, the strong central feature due to the tungsten isotopes with $I = 0$ is split into four lines when the magnetic field is within ±30° of a^* in the *ac* plane. This splitting is consistent with an interaction with a single chlorine atom. Spectra with the magnetic field parallel to a^*, b, and c are shown in Figure 4. The measured principal crystal *g* values obtained from these spectra (Table IV) are similar to those found[2] from both the powder and frozen solution spectra for the comparable anion $[Cl_3W(\mu\text{-}SPh)_2(\mu\text{-}Cl)WCl_3]^{2-}$ of **3**. For these reasons, we attribute the ESR spectra of **1** to the co-crystallization of the anion of **2** in the same lattice, and we qualitatively assign the principal crystal *g* values to principal molecular *g* values. (Figures 1b and 3). This assignment assumes that the W–W vector is parallel to the crystal *c* axis and that the W–Cl–W plane is parallel to *b*. In practice the W–W vector makes an angle of 5.4° with *c*, while the normal to the W–Cl–W plane makes an angle of 5.5° with a^*. These deviations mean that we have underestimated g_{zz} by ca. 0.2%, and overestimated g_{xx} and g_{yy} by ca. 0.4%. However, the anisotropy will remain qualitatively the same. Such an assignment of the *g* values in **3** could not possibly be made with such certainty.[2] Also, the powder and frozen-solution measurements on **3** did not give any indication of ^{183}W or $^{35,37}Cl$ hyperfine interactions.

We previously interpreted the ESR data of **3** in terms of a qualitative molecular orbital model for a M_2L_9 species with C_{2v} point symmetry, following the approach of Summerville and Hoffmann.[3] In that treatment, the *g* values were shown to be consistent with either of the ground-state configurations, $(1A_1)^2(1B_1)^2(2A_1)^1$ or $(1A_1)^2(2A_1)^2(1B_1)^1$ (see Figure 5 in ref 1). Qualitatively the magnitudes and orientations of the *g* values in **2** reinforce this interpretation, but because of the large number of parameters involved, it is still not realistic to give a numerical interpretation of the data. However, the observation of tungsten hyperfine splittings and of hyperfine interactions with one chlorine atom provides some additional qualitative information concerning the electronic structure. These observations reinforce the view that the unpaired electron is mainly associated with the bridging region of the anion. Furthermore, the observation that the maximum chlorine hyperfine splitting is associated with the *x* direction (crystal direction a^*, see Figure 1b) enables us to make a distinction between the two possible ground-state configurations. For an electron in a chlorine p_x orbital, we would expect the magnitude of the anisotropic part of the hyperfine splitting parallel to *x* to be twice that of the other principal values.[15] This is approximately what we find, and hence our observations strongly implicate the involvement of the chlorine p_x orbital in the ground-state wave functions. In C_{2v} point symmetry and with the molecular axis system in Figure 1b, the chlorine p_x, p_y, and p_z orbitals transform as b_1, a_1, and b_2, respectively. Thus the chlorine p_x orbital will be involved with the metal molecular orbital system, which has B_1 symmetry. Hence, the ESR results are consistent with the ground-state configuration $(1A_1)^2(2A_1)^2(1B_1)^1$.

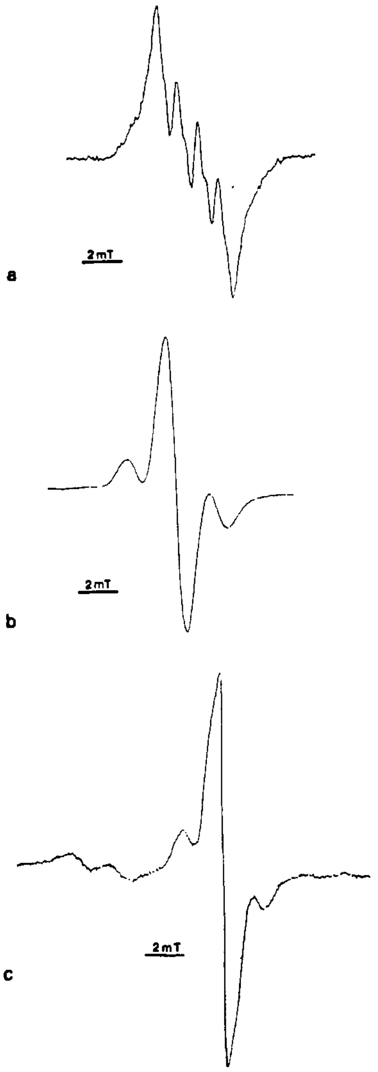

Figure 4. Single-crystal ESR spectra of $[PPh_4]_2[Cl_3W\{\mu\text{-}Se(Cl)\}(\mu\text{-}SePh)_2WCl_3]\cdot 2CH_2Cl_2$ (**1, 2**) at 77 K, ν = 9.269 GHz, with the magnetic field parallel to (a) a^*, (b) b, and (c) c crystal axes.

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Supplementary Material Available: Tables SI–IV, respectively listing complete X-ray data, the calculated hydrogen atom positions, anisotropic thermal parameters for the non-hydrogen atoms, and complete bond lengths and bond angles, and Figure S1, a stereoview of the contents of the unit cell (7 pages); Table SV, listing the observed and calculated structure factors (73 pages). Ordering information is given on any current masthead page.

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(15) Wertz, J. E.; Bolton, J. R. *Electron Spin Resonance, Elementary Theory and Practical Applications*; Chapman and Hall: London, 1986; p 171.