Synthesis and Characterization of the Heterometallic Complexes (PPh₄)₂[Mn(MS₄)₂] (M = Mo, W). X-ray Crystal Structure of the Tungsten Derivative

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Heterometallic complexes of the type $[M'(MS_4)_2]^{2-}$ (M = Mo, W; M' = Fe, Co, Ni, Zn) were isolated some years ago as salts of bulky countercations by reaction, in aqueous solution, of 3d metal ions with the tetrathiometalate species. These complexes, which are interesting from the structural point of view and/or have unusual electronic properties, have been intensively investigated.[1] However any attempt to prepare the manganese(II) representatives so far has failed, even though recently the related compounds [(bipy)₂Mn(MS₄)] were reported.[2] We have now had success in the preparation of the title complexes by simply reacting manganese(II) bromide with molybdenum or tungsten tetrathiometalates in methanol solution. The complexes have been characterized by magnetic and spectroscopic (IR, visible–UV, EPR) measurements. A complete X-ray analysis of the compound (PPh₄)₂[Mn(WS₄)₂] has been carried out, and its electronic structure has been investigated by using Xα–SW calculations.

Experimental Section

Synthesis. All reactions and manipulations were routinely carried out under a nitrogen atmosphere. The solvents used were analytically pure and were dried over molecular sieves. Literature routes were used for the preparation of (PPh₄)₂MS₄ (M = Mo, W).[3] MnBr₂ was purchased from Fluka and used without further purification.

(PPh₄)₂[Mn(MoS₄)₂] (1). A solution of 0.45 g (0.5 mmol) of (PPh₄)₂-MoS₄ in 30 mL of methanol was added, at room temperature, to a solution of 0.054 g (0.25 mmol) of MnBr₂ in 10 mL of the same solvent. The color of the solution changed immediately from red-brown to dark-brown. Slow diffusion of diethyl ether (30 mL) through the solution allowed the precipitation of dark-brown crystals. These were filtered off, washed with ether, and dried under a current of nitrogen; yield 0.24 g (81%). Anal. Calcd for C₄₈H₄₀Mo₂MnP₂S₈: C, 48.77; H, 3.41; Mn, 4.66. Found: C, 48.62; H, 3.50; Mn, 4.48. IR data (ν(MS) region): 502, 479 (ν(MSₜ)), 452, 440 cm⁻¹ (ν(MSᵦ)) (t = terminal; b = bridging). Visible spectrum: reflectance, 530 (sh), 460, 370 nm (sh); in MeOH, 530 (sh), 467.5 (ε 15 320), 365 (sh), 318 nm (27 690); in DMF, 535 (sh), 469 (ε 17 150), 360 (sh), 321 nm (31 340) [the parent (MoS₄)²⁻ in DMF, 534 (sh), 477 (ε 15 670), 360 (sh), 325 nm (20 110)].

(PPh₄)₂[Mn(WS₄)₂] (2). The complex was prepared in a manner quite similar to that for the previous compound. Deep-brown crystals were obtained; yield 85%. Anal. Calcd for C₄₈H₄₀MnP₂S₈W₂: C, 42.45; H, 2.97; Mn, 4.05. Found: C, 42.34; H, 3.05; Mn, 3.95. IR data (ν(MS) region): 500, 487, 478, 464 (ν(MSₜ)), 446, 427 cm⁻¹ (ν(MSᵦ)). Visible

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Table I. Crystallographic Data

formula	C₄₈H₄₀MnP₂S₈W₂	D_{calc}, g cm⁻³	1.862
fw	1357.9	μ(Mo Kα), cm⁻¹	55.2
a, Å	13.191 (4)	transm coeff	0.95–1.12
c, Å	6.959 (1)	T, °C	22
V, Å³	1210.9	λ, Å	0.7107
Z	1	R, Rₐ[a]	0.028, 0.028
space group	I4̄ (No. 82)		

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = \{[\sum w(|F_o| - |F_c|)^2]/[\sum w|F_c|^2]\}^{1/2}$.

Table II. Final Atomic Parameters[a]

atom	x	y	z	U or U_{eq}, Å²	PP
Mn	0	0	0	44 (2)[b]	0.125
W	0	0	4392 (2)	27 (2)[b]	0.250
P	5000	0	2500	31 (2)[b]	0.250
S(1)	1278 (5)	389 (5)	2449 (10)	42 (4)[b]	0.500
S(2)	−387 (5)	1286 (6)	6169 (11)	50 (5)[b]	0.500
C(1)	4023 (5)	461 (3)	947 (12)	34 (2)	1.0
C(2)	3557 (5)	−227 (3)	−294 (12)	44 (3)	1.0
C(3)	2782 (5)	97 (3)	−1513 (12)	56 (3)	1.0
C(4)	2474 (5)	1109 (3)	−1491 (12)	64 (4)	1.0
C(5)	2940 (5)	1796 (3)	−251 (12)	57 (3)	1.0
C(6)	3714 (5)	1473 (3)	968 (12)	39 (3)	1.0

[a] Thermal parameters multiplied by 10³; coordinates by 10⁴. [b] U_{eq} defined as one-third of the trace of the orthogonalized thermal tensor.

spectrum: reflectance, 430 (sh), 400 nm; in MeOH, 440 (sh), 393 (ε 17 140), 325 (sh), 285 nm (18 080); in DMF, 435 (sh), 396 (ε 11 460), 330 (sh), 275 nm (72 000) [the parent (WS₄)²⁻ in DMF, 435 (sh), 400.5 (ε 8740), 330 (sh), 283.5 nm (22 110)].

[(Fe,Mn)(DMF)₆][Cl₂FeS₂WS₂] (3). A solution of 0.115 g of anhydrous FeCl₂ (0.9 mmol) in 15 mL of DMF was added, at room temperature, to a solution of 0.41 g of 2 (0.3 mmol) in 25 mL of DMF. Slow diffusion of ether through the resulting red-orange solution afforded red-orange crystals; yield 0.35 g (62%). Anal. Calcd for C₃₆H₈₄N₁₂Cl₄Fe₃MnO₁₂-S₈W₂: C, 23.16; H, 4.54; N, 9.0; Fe, 9.0; Mn, 2.95. Found: C, 23.04; H, 4.53; N, 8.91; Fe, 8.95; Mn, 2.74.

Physical Measurements. IR spectra, as Nujol mulls, were recorded on a Perkin-Elmer 1600 FTIR spectrophotometer. Reflectance and solution electronic spectra were recorded on Beckman DK-2A and Shimadzu UV-2100 spectrophotometers, respectively. Magnetic susceptibility measurements were carried out, at room temperature, on a Faraday balance. EPR spectra of (PPh₄)₂[Mn(WS₄)₂] were recorded in the temperature range 4.2–300 K both on the polycrystalline samples and in methanol and DMF solutions, using a Varian E9 spectrometer equipped with an Oxford Instruments continuous-flow cryostat.

Collection and Reduction of the X-ray Data. A deep-brown irregular prism of approximate dimensions 0.15 × 0.10 × 0.05 mm was mounted on an Enraf-Nonius CAD4 automatic diffractometer. The unit cell constants were determined by a least-squares treatment of the setting angles of 25 reflections. The crystals belong to the tetragonal system, with systematic absences $h + k + l = 2n + 1$ for hkl. Due to the isomorphism of the title compound with the [Zn(WS₄)₂]²⁻ compound,[4] the acentric space group I4̄ was chosen and then confirmed by the successful refinement of the structure. Intensity data were collected by the ω–2θ scan method (5 ≤ 2θ ≤ 50°) using graphite-monochromatized Mo Kα radiation. Three check reflections measured every 2 h showed no significant intensity reduction. After correction for backgrounds, the standard deviations σ(I) were calculated, as described elsewhere,[5] by using the value of 0.03 for the instability factor k. Data were corrected by Lorentz–polarization effects and for absorption.[6] Crystal data are summarized in Table I.

All the calculations were carried out on a HP 486 PC, by using the SHELX76[7] and ORTEP[8] programs. Atomic scattering factors for the

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Scheme I
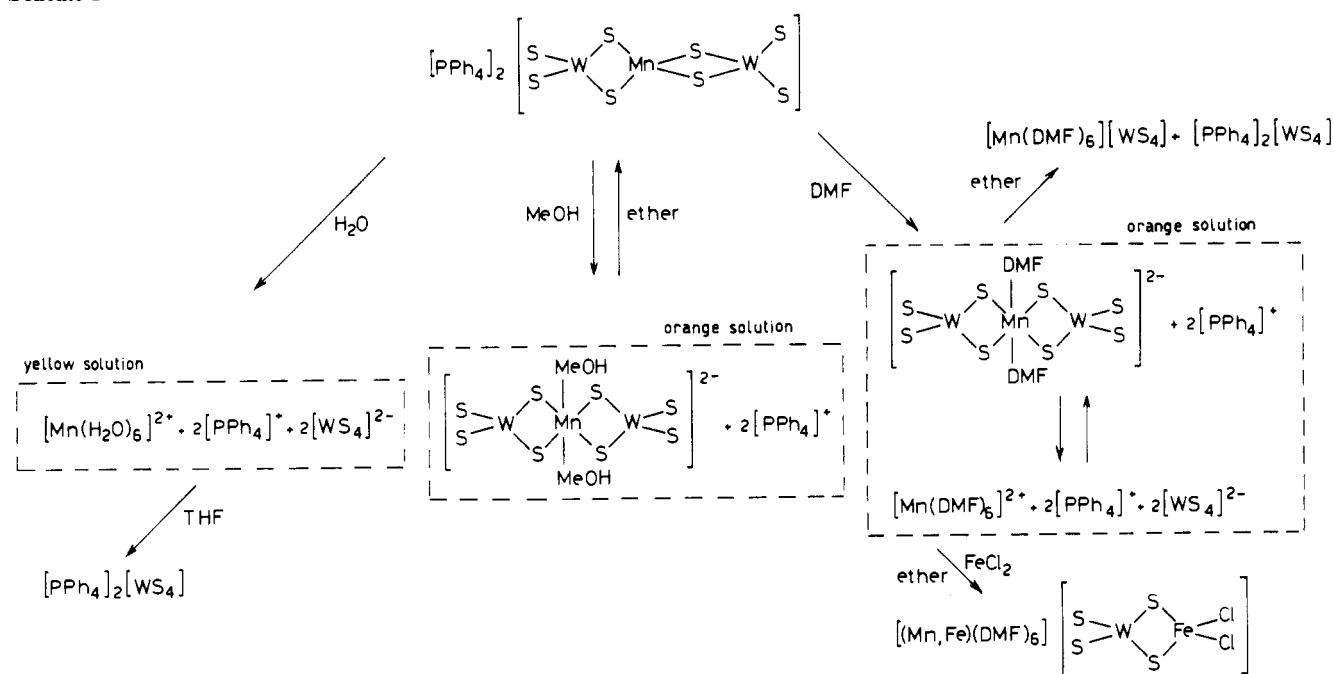
appropriate neutral atoms were taken from ref 9 for hydrogen and from ref 10 for non-hydrogen atoms. Both $\Delta f'$ and $\Delta f''$ components of the anomalous dispersion were included for the non-hydrogen atoms.[11] The structure was solved with the help of the known atom positions of the isomorphous $[Zn(WS_4)_2]^{2-}$ compound.[4] Since the number of equivalent positions in the $I\bar{4}$ space group is at least 2 and there is only one formula unit of $(PPh_4)_2[Mn(WS_4)_2]$ per unit cell, a disorder situation for the anion has to be expected. A detailed crystallographic rationalization and description of such a disorder has been reported in the work of Müller et al.[4] Full-matrix least-squares refinements were carried out by assigning anisotropic thermal parameters to manganese, tungsten, sulfur, and phosphorus atoms. The function minimized was $\sum w(|F_o| - |F_c|)^2$, w being set equal to $1/\sigma^2(F_o)$. The phenyl rings were treated as rigid bodies of D_{6h} symmetry. Hydrogen atoms were introduced in calculated positions and not refined. The refinement converged to R and R_w factors both equal to 0.028. Final atomic parameters are given in Table II.

Xα-SW Calculations. Xα-SW calculations[12] were performed for $(PPh_4)_2[Mn(WS_4)_2]$ in D_{2d} symmetry using the bond distances and angles seen in the crystal structure. The calculations were performed using the COOK5/TAMU1 program written by M. Cook, B. Bursten, and G. Stanley. The sphere radii were computed using the Norman procedure[13] taking 88% of the free-electron radius to avoid excessive overlap between the atomic spheres. The computed sphere radii are $R(Mn) = 2.600$ Å, $R(W) = 2.537$ Å, $R(S_t) = 2.500$ Å, and $R(S_b) = 2.488$ Å, where S_t and S_b are the terminal and bridging sulfur atoms, respectively. A tangent Watson sphere,[14] with charge opposite to that of the molecule, was placed around the molecule to mimic the counterion environment. The largest values of l used were $l = 4$ for the outer-sphere region, $l = 2$ for Mn, $l = 3$ for W, and $l = 1$ for S. The atomic values of α tabulated by Schwarz for the free atoms[15] were used in the atomic spheres. The α value for the intersphere and outer-sphere regions was determined by averaging the values used in the atomic spheres, weighted by the number of the atomic valence electrons. Core levels are assumed to be confined in the atomic spheres and included in the self-consistent procedure.

Results and Discussion

By reaction of anhydrous manganese(II) halides with $(PPh_4)_2$-(MS_4) (M = Mo, W), in a 1:2 ratio in methanol/ether solution, crystals of $(PPh_4)_2[Mn(MS_4)_2]$ (M = Mo, **1**; M = W, **2**) are formed in good yield. The complexes can be quantitatively recrystallized from methanol/ether solutions. The IR spectrum of **1** (Nujol mulls) exhibits in the $\nu(MS)$ region bands at 502, 479, 452, and 440 cm⁻¹, attributable to the $\nu(MS_t)$ and $\nu(MS_b)$ vibrations.[16] The IR spectrum of **2** shows a similar pattern with the first two bands split to form a couple of doublets. The visible

reflectance spectra of the two complexes are analogous to the corresponding spectra in solution (MeOH, DMF). They essentially show transitions corresponding to those of the free thiometalate ions.[1] It is worth noting that whereas the bands undergo only minor shifts, these are remarkably enhanced by complex formation (see Experimental Section). The magnetic moments of complexes **1** and **2**, at room temperature (5.64 and 5.68 μ_B, respectively), indicate that these species are characterized by five unpaired electrons.

Dissolution of **2** in water gave a yellow solution whose visible spectrum is identical to that of $(PPh_4)_2(WS_4)$ in the same solvent. Addition of THF to this solution allowed the precipitation of yellow crystals of the parent tetrathiometalate, which was identified by the IR spectrum. Complex **1** had an analogous behavior. Hydrolysis of **1** and **2** similarly occurs also in methanol solution when a few drops of water are added. This finding well accounts for the failure in the synthesis of the complexes by reaction of hydrated manganese(II) halides with tetrathiometalates in aqueous solutions. Some solvolysis of the title complexes likely occurs also in strongly coordinating organic solvents. Indeed, the orange solutions of **2** in DMF, which practically display the same electronic spectra as the corresponding methanol solutions, after ether addition, afford yellow crystals which on the basis of elemental analysis and IR spectra have been identified as a mixture of $(PPh_4)_2(WS_4)$ and $[Mn(DMF)_6](WS_4)$.[17] The solvolysis of **2** in DMF was corroborated by the reaction of **2** with $FeCl_2$ in this solvent, which allowed the synthesis of the multimetallic complex $[(Fe,Mn)(DMF)_6][Cl_2FeS_2WS_2]$ (**3**)

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(17) The IR spectrum of a sample of this yellow product shows in the region of the W–S stretching vibrations only a band at 454 cm⁻¹ due to the $\nu(W–S_t)$ of uncoordinated WS_4^{2-}. Moreover, the spectrum shows a strong band at 1652 cm⁻¹ attributable to the CO stretching vibration of coordinated DMF.
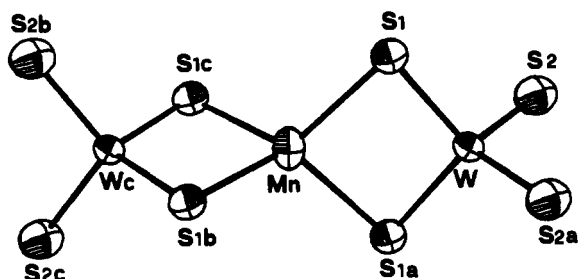
Figure 1. Perspective view of the complex anion $[Mn(WS_4)_2]^{2-}$ (ORTEP drawing with 30% probability ellipsoids).

Table III. Selected Bond Distances (Å) and Bond Angles (deg)[a]

Mn–S(1)		W–S(1)	
Mn–S(1a)	2.452 (7)	W–S(1a)	2.222 (7)
Mn–S(1b)		W–S(2)	
Mn–S(1c)		W–S(2a)	2.161 (7)
Mn···W	3.056 (1)		
S(1)–Mn–S(1a)	91.9 (2)	S(1)–W–S(2)	110.3 (3)
S(1b)–Mn–S(1c)		S(1a)–W–S(2a)	
S(1)–Mn–S(1b)		S(1)–W–S(2a)	110.5 (3)
S(1)–Mn–S(1c)	118.9 (2)	S(2)–W–S(1a)	
S(1a)–Mn–S(1b)		S(1)–W–S(1a)	105.0 (3)
S(1a)–Mn–S(1c)		S(2)–W–S(2a)	110.2 (3)
Mn–S(1)–W	81.5 (2)		

[a] Symbols a, b, and c refer to the following symmetry operations: (a) $-x, -y, z$; (b) $y, -x, -z$; (c) $-y, x, -z$.

(Scheme I). The formulation of **3** was inferred from elemental analysis and preliminary X-ray data results.[18] The structures of related compounds such as $[Fe(DMF)_6][Cl_2FeS_2WS_2]$ and $(PPh_4)_2[Cl_2FeS_2WS_2]$ had been previously reported.[1a]

Description of the Structure. The crystal structure of **2** consists of discrete $[Mn(WS_4)_2]^{2-}$ anions and PPh_4^- cations. Figure 1 shows a perspective view of the complex anion, whose selected distances and angles are given in Table III. In the $[Mn(WS_4)_2]^{2-}$ anion, which is isostructural with the zinc analogue, the manganese center is surrounded by four sulfur atoms belonging in pairs to two WS_4 fragments; the geometry of the manganese atom is distorted tetrahedral, as the S–Mn–S angles vary from 91.9 (2) to 118.9 (3)°. Also, the tungsten centers display tetrahedral environments with S–W–S angles very close to the ideal values (105.0 (3)–110.5 (3)°). The four-membered rings MnS_2W are strictly planar, as required by the $\bar{4}$ site symmetry of the anion. The Mn–S bonds are equal in length, and the W–S (bridging and terminal) bonds are equal in pairs of two. The four-membered MnS_2W ring appears somewhat strained, this strain being reflected in the Mn–S bond distance: as a matter of fact, while the W–S distances display values [2.161 (7) (terminal) and 2.222 (7) Å (bridging) (average 2.19 Å)] in agreement with those reported for the free anion,[19] the Mn–S bond of 2.452 (7) Å is significantly larger than the sum of covalent radii (2.19 Å) and somewhat larger than the corresponding bond (2.392 (5) Å) in the Zn analog.[4] As a consequence, also the Mn···W separation of 3.056 (1) Å is slightly larger than the value of 2.927 (1) Å found in the $[Zn(WS_4)_2]^{2-}$ derivative, these differences likely being attributable to the large size of the manganese(II) ion in the high-spin configuration.

EPR. Polycrystalline EPR spectra of **2** recorded at 300 and 4.2 K are shown in Figure 2, and frozen-solution spectra, of the same compound, recorded at 4.2 K are shown in Figure 3. The polycrystalline spectra are typical of a high-spin manganese(II)
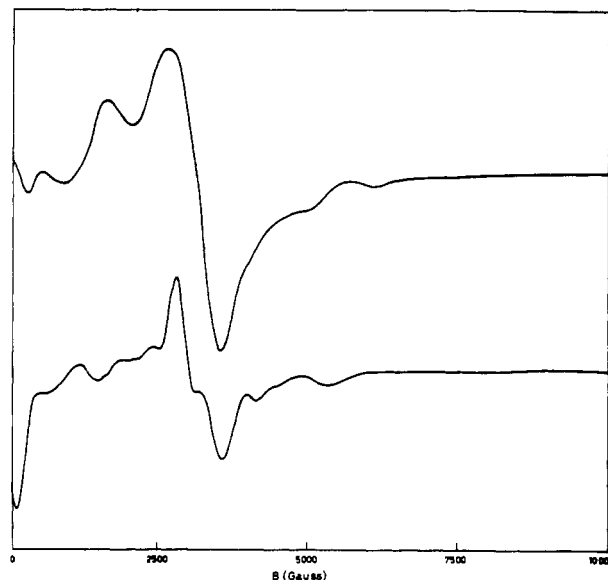
(18) Triclinic, $P1$, $a = 11.367$ (8) Å, $b = 9.820$ (6) Å, $c = 8.754$ (6) Å, $\alpha = 83.39$ (9)°, $\beta = 74.98$ (8)°, $\gamma = 71.58$ (8)°. The structure consists of $[(Fe,Mn)(DMF)_6]^{2+}$ cations and $[Cl_2FeS_2WS_2]^{2-}$ anions. In the cation, the metal center is statistically iron or manganese. In the anion, $FeCl_2$ and WS_2 moieties are bridged by two sulfur atoms.

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Figure 2. Polycrystalline EPR powder spectra recorded at 300 K (upper) and 4.2 K (lower) for $(PPh_4)_2[Mn(WS_4)_2]$.

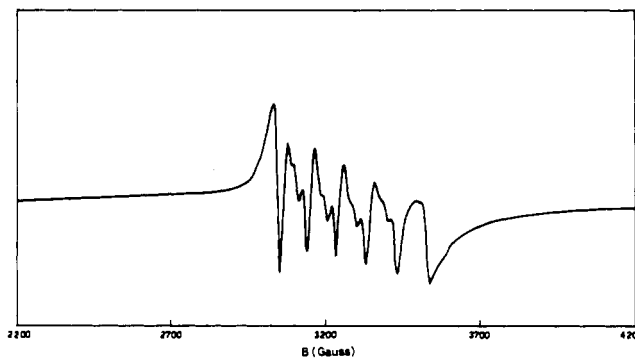**Figure 3.** Frozen-solution EPR spectrum recorded at 4.2 K for $(PPh_4)_2$-$[Mn(WS_4)_2]$.

complex[20] showing transitions between an $S = 5/2$ spin manifold split in zero field. The symmetry of the complex requires that the zero-field-splitting tensor be axial, and the appearance of a transition at low-field values is consistent[21] with D values in the ranges 0.06–0.09 cm^{-1} and 0.14–0.17 cm^{-1}. The spectrum recorded at 300 K differs from that recorded at 4.2 K, showing that the zero-field splitting is temperature dependent. A detailed analysis of the spectra is outside the purpose of this paper. The frozen-solution spectra both in DMF and in methanol show a six-line signal centered at $g = 2.00$ with $A = 84$ G and rather intense forbidden $\Delta M_I = 1$ transitions. This spectrum is consistent with an $S = 5/2$ spin Hamiltonian split by a rather small zero-field splitting ($D < 10^{-3}$ cm^{-1}). These results show that in solution the symmetry around manganese(II) is higher than the symmetry found in the solid state. A high symmetry was also found in the related complex $[(bpy)_2Mn(WS_4)]$.[2c]
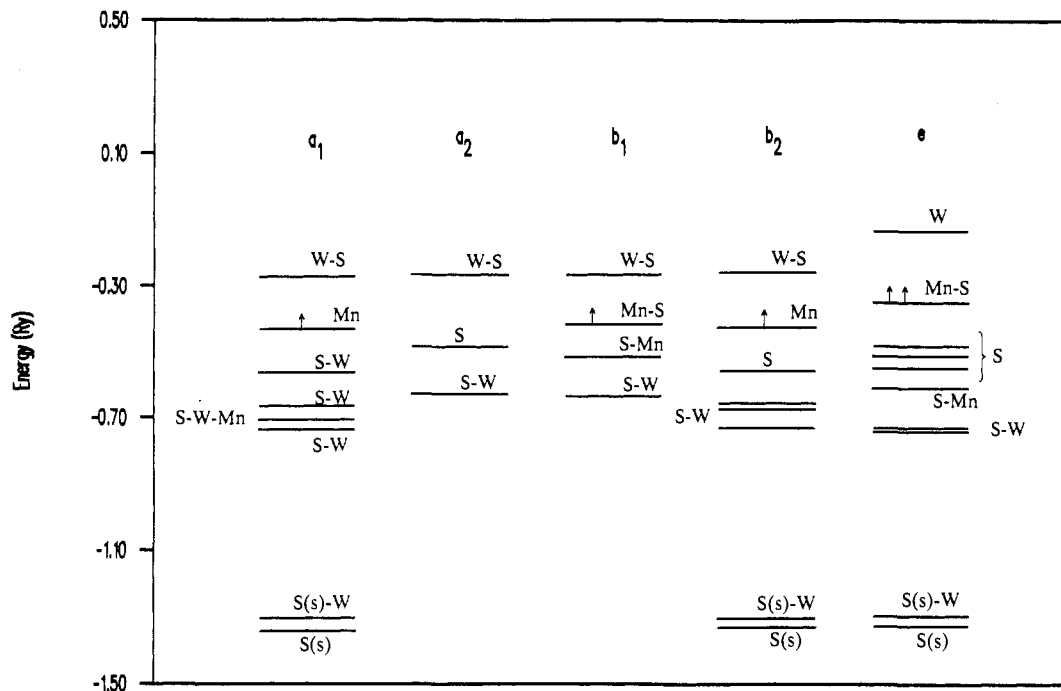
Calculations. The energy levels computed by using spin-restricted $X\alpha$–SW theory are shown in Figure 4. The levels are labeled according the irreducible representations of the D_{2d} point symmetry group, and the relevant Mn, W, or S components are shown. Nine orbitals are expected to be sulfur p nonbonding (when only nearest-neighbor interactions are considered), belonging to the symmetry species $a_1 + a_2 + b_2 + 3e$ and correspond to the $6a_1$, $2a_2$, $6b_2$, $6e$, $7e$, and $8e$ molecular orbitals in Figure 4. The highest occupied molecular orbitals are mainly Mn(3d) in character, and the ground-state configuration of the molecule

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Figure 4. Highest occupied and lowest unoccupied energy levels for $(PPh_4)_2[Mn(WS_4)_2]$ computed using the RHFS–Xα–SW technique. The largest atomic contributions to the molecular orbitals are indicated. The levels are labeled according to the D_{2d} point group. The HOMO's are indicated with arrows.

can be written $^6A_1(7a_1{}^13b_1{}^17b_2{}^19e^2)$. The lowest unoccupied molecular orbitals are all W(3d) in character. The gross atomic populations computed by the charge-partitioning technique of Case, Cook, and Karplus[22] are very close to neutrality, being $-0.11, 0.54, -0.42$, and -0.27 for Mn, W, S_t, and S_b, respectively. These results closely follow those found for other $[M'(MS_4)_2]^{n+}$ (M = Mo, W; M' = Fe, Ni, Pd, Pt) complexes.[23–25]

Conclusions

Complexes 1 and 2 can be cleanly synthesized in methanolic solutions. As inferred from the IR data and fully confirmed by X-ray analysis, the manganese centers are tetrahedral in the solid state. The compounds undergo rapid hydrolysis in aqueous solutions, to re-form the parent tetrathiometalates. In both methanol and DMF anhydrous solutions of 2, on one hand, the

color and the features of the visible spectra suggest the coordination of the $(WS_4)^{2-}$ species to the manganese ion and, on the other hand, the EPR spectra indicate the manganese ion to have symmetry higher than that found in the solid state. Moreover, whereas 2 is recovered unchanged from methanol solutions, products containing the species $[Mn(DMF)_6]^{2+}$ have been isolated from DMF. Scheme I may be proposed to account for these processes. The further coordination of two solvent molecules to the tetracoordinated M' center in $[M'(MS_4)]^{2-}$ species to obtain an octahedral environment had been previously reported for M = Fe.[1a,26]

Supplementary Material Available: Tables of crystallographic details, anisotropic thermal parameters, hydrogen atom coordinates, and bond distances and angles (4 pages). Ordering information is given on any current masthead page.

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