The initial condition, [I] = $[\mathrm{I}]_0$ at $t = 0$, leads to the coefficients

$$a_0 = 1$$
$$a_1 = -(k_7 + k_8 + 2k_9[\mathrm{I}]_0)$$
$$a_2 = {}^1\!/_2 a_1{}^2 ...$$
$$a_3 = {}^1\!/_6 a_1{}^3 ...$$

Series describing the time dependences of the radical concentration and optical density were obtained by a similar treatment.[11] The corresponding series for the change in the optical density, ΔOD, is

$$\Delta\mathrm{OD_p}(t) = [\Delta\mathrm{OD_p}(0)]\left[1 - \left(k_7 - \frac{k_9[\Delta\mathrm{OD_p}(0)]}{\epsilon l}\right)t - \left(\frac{k_7}{2} - \frac{k_9[\Delta\mathrm{OD_p}(0)]}{\epsilon l}\right)a_1 t^2 - ...\right]$$

This expression was recast in the form

$$\frac{\Delta\mathrm{OD_p}(0) - \Delta\mathrm{OD_p}(t)}{t[\Delta\mathrm{OD_p}(0)]} \approx k_7 - \frac{k_9}{\epsilon l}\Delta\mathrm{OD_p}(0)$$

for the graphic representation of the experimental data (Figure 2). Moreover, the values of k_7 and k_9 together with values for the initial and final $\Delta\mathrm{OD_p}$, e.g. ΔOD(0) and ΔOD(∞), were used for the calculation of k_8.

Registry No. pc, 574-93-6; Rh(pċ)Br$^+$, 105900-44-5; Rh(pċ)Cl$^+$, 105900-45-6; Al(pċ)Cl$^+$, 57650-26-7; Zn(pċ)$^+$, 53029-44-0.

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(11) The extinction coefficient of the intermediate I has been regarded to be insignificant in relationship to the extinction coefficient of M(pċ)$^+$, a proposition that is in agreement with the structure proposed for I.

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Synthesis and Structure of $[\mathrm{W_2(S)_2(\mu\text{-}S)(\eta^2\text{-}S_2)_4}]^{2-}$, a Novel Binary Sulfide Derived from the Acidification of $\mathrm{WS_4}^{2-}$

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$[\mathrm{M'(MS_4)_2}]^{2-}$ complexes (with M = Mo, W and M′ = Zn, Ni, Fe, Co, Pd, Pt)[1] have been synthesized, and structural determinations by X-ray diffraction have been reported for these complexes. In an attempt to prepare the $[\mathrm{Mn(MS_4)_2}]^{2-}$ dianion, we have isolated with M = W a dark red crystalline material that was identified by elemental analysis as an unexpected new tungsten sulfide.

The synthesis of the molybdenum analogue was not successful; instead, we isolated the anion $\mathrm{Mo_3S_9}^{2-}$.[2] Here we report the synthesis, isolation, and structural characterization of a new binary W–S complex.

Experimental Section

All manipulations were carried out in air; chemicals were used as purchased.

$(\mathrm{PPh_4})_2\mathrm{W_2S_{11}}$. A solution of 0.375 g (0.38 mmol) of $(\mathrm{PPh_4})_2\mathrm{WS_4}$ in 32 mL of $\mathrm{CH_3CN}$ was acidified with 0.15 mL of glacial acetic acid. After addition of a solution of 0.15 g (0.75 mmol) of $\mathrm{MnCl_2{\cdot}4H_2O}$[3] in 2 mL of $\mathrm{CH_3OH}$ the mixture turned immediately deep red. The resulting solution was stirred for 1 h, allowed to stand ca. 1 h at room temperature, and then filtered and cooled in a closed flask under argon to −10 °C. After 24 h analytically pure, well-shaped, large dark red crystals were obtained (70 mg), which were separated from the filtrate, washed with small amounts of ether, and air-dried. Anal. Calcd for $\mathrm{C_{50}H_{43}NP_2W_2S_{11}}$: C, 41.7; S, 24.5; P, 4.3; W, 25.5. Found: C, 40.8; S, 25.9; P, 4.3; W, 25.1.

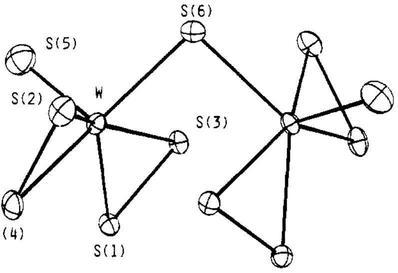

Figure 1. Perspective view (50% ellipsoids) of the $\mathrm{W_2S_{11}}^{2-}$ anion showing the atom-labeling scheme. Half of the anion is generated through a binary axis passing through the S(6) atom.

$(\mathrm{PPh_4})_2\mathrm{Mo_3S_9}$. This complex was prepared in a manner similar to that for the previous one. Within 1–3 days at −10 °C, dark red needlelike crystals were obtained. The IR spectra and the X-ray space group of the compound were identical with those of $(\mathrm{PPh_4})_2\mathrm{Mo_3S_9}$.[2]

Physical Measurements. Electronic spectra were recorded at 20 °C on a Kontron 810 spectrophotometer between 600 and 200 nm. Solutions of the compound in $\mathrm{CH_3CN}$ were about 1 mg mL^{-1}. Infrared spectra (KBr pellet) were recorded on a Perkin-Elmer 580B spectrophotometer.

Crystal Structure Determination. The unit cell dimensions and space group were determined from preliminary oscillations and Weissenberg photographs. The symmetry was monoclinic, and the systematic absences led to the *C*2/*c* or *Cc* space group. A single crystal of dimensions 0.12 × 0.17 × 0.34 mm was selected and mounted on a Nonius CAD 4 automatic diffractometer equipped with Mo Kα radiation and a graphite monochromator. Least-squares calculations on 25 high-angle reflections collected at 20 °C yielded a monoclinic cell of dimensions a = 20.724 (6) Å, b = 20.367 (3) Å, c = 12.452 (3) Å, β = 99.52 (2)°, and V = 5183 Å^3.

Other details of data collection were as follows: scan mode $\theta/2\theta$, scan rate variable, scan range calculated by 1.00 + 0.34 tan θ with 25% extension on each side for backgrounds. Three orientation standards were checked every 100 observations. Three intensity monitors were checked every hour and remained constant. The calculated density was 1.85 g cm^{-3} with Z = 4 formula units per cell. A total of 5284 reflections ($\pm h,+k,+l$) were measured up to $\theta_{\max}$ = 25°; after averaging 4207 were obtained, and among them, 3224 with $F_o > 4\sigma(F_o)$ were the final data set. Lorentz and polarization corrections were applied to the data. No absorption correction was made.

The centrosymmetric space group *C*2/*c* was first assumed and gave satisfactory refinement. The structure was solved by the heavy-atom method. A three-dimensional Patterson map revealed the position of the tungsten atom. Successive refinements and difference Fourier maps revealed the locations of the remaining atoms (S, P, and C of the phenyl rings). The refinement with isotropic thermal parameters for all located atoms gave a R value of 0.098 for 2957 observations. At this stage a difference Fourier exhibited peaks that were attributed to a solvent molecule ($\mathrm{CH_3CN}$). Riding isotropic hydrogen atoms were included in the refinement subject to the constraints C–H = 1.08 Å and U(H) = 1.1[U(C)], where U(C) is the equivalent isotropic thermal parameter of a carbon atom of the phenyl ring. Additional cycles of refinement with anisotropic temperature factors for W, P, and S and isotropic thermal parameters for all other atoms converged to conventional values of R = 0.0402 and R_w = 0.036 with a GOF of 0.67. All computations were performed by using SHELX76 on a Gould Concept 32/87 computer. Neutral atomic scattering factors and correction for anomalous dispersion were obtained from ref 4. Final atomic positional parameters were found

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[‡] Laboratoire de Chimie des Métaux de Transition.

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(3) At the suggestion of a reviewer we have shown from complementary experiments that a methanolic solution of LiCl leads to the formation of only $\mathrm{W_3S_9}^{2-}$. Furthermore, a solution of $\mathrm{CrCl_3}$ produces only $\mathrm{W_4S_{12}}^{2-}$. These results are consistent with the need for $\mathrm{MnCl_2}$ to synthesize $\mathrm{W_2S_{11}}^{2-}$.

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Table I. Positional Parameters and Standard Deviations for the Atoms of $[P(C_6H_5)_4]_2[W_2S_{11}]\cdot CH_3CN$

atom	*x/a*	*y/b*	*z/c*
W	0.48156 (2)	0.19210 (2)	0.38191 (3)
S(1)	0.4447 (1)	0.0827 (1)	0.3447 (2)
S(2)	0.5796 (1)	0.2366 (1)	0.4824 (2)
S(3)	0.4170 (1)	0.1477 (1)	0.2198 (2)
S(4)	0.5505 (1)	0.1472 (2)	0.5394 (2)
S(5)	0.4088 (2)	0.2344 (2)	0.4545 (3)
S(6)	0.5000	0.2772 (2)	0.2500
P	0.7835 (1)	0.0486 (1)	0.4022 (2)
C(11)	0.7899 (4)	0.1002 (4)	0.5205 (7)
C(12)	0.7436 (4)	0.1504 (5)	0.5207 (7)
C(13)	0.7491 (4)	0.1929 (5)	0.6074 (7)
C(14)	0.8018 (5)	0.1866 (5)	0.6914 (8)
C(15)	0.8474 (5)	0.1383 (5)	0.6913 (9)
C(16)	0.8415 (4)	0.0948 (5)	0.6050 (8)
C(21)	0.7791 (4)	0.1011 (4)	0.2858 (7)
C(22)	0.7310 (5)	0.0929 (5)	0.1958 (8)
C(23)	0.7281 (6)	0.1337 (6)	0.108 (1)
C(24)	0.7731 (7)	0.1828 (7)	0.112 (1)
C(25)	0.8222 (6)	0.1946 (8)	0.203 (1)
C(26)	0.8238 (5)	0.1533 (5)	0.2911 (9)
C(32)	0.6581 (4)	0.0129 (4)	0.4338 (7)
C(33)	0.6019 (5)	−0.0249 (5)	0.4086 (8)
C(34)	0.6011 (5)	−0.0773 (6)	0.3395 (9)
C(35)	0.6536 (5)	−0.0926 (5)	0.2942 (9)
C(36)	0.7098 (5)	−0.0555 (5)	0.3154 (8)
C(41)	0.8544 (4)	−0.0035 (5)	0.4138 (7)
C(42)	0.9067 (4)	0.0097 (5)	0.3619 (8)
C(43)	0.9601 (5)	−0.0305 (5)	0.3783 (9)
C(44)	0.9600 (6)	−0.0862 (6)	0.4415 (9)
C(45)	0.9093 (6)	−0.0987 (6)	0.494 (1)
C(46)	0.8570 (5)	−0.0566 (5)	0.4820 (9)
N	0.0000	0.1221 (9)	0.2500
C(1)	0.0000	0.1770 (7)	0.2500
C(2)	0.0000	0.249 (1)	0.2500

Table II. Bond Lengths (Å) and Angles (deg) for $[W_2S_{11}]^{2-}$[a]

W–S(1)	2.376 (2)	W–S(4)	2.407 (3)
W–S(2)	2.382 (3)	W–S(5)	2.070 (4)
W–S(3)	2.407 (2)	W–S(6)	2.461 (2)
S(1)–S(3)	2.050 (3)	S(2)–S(4)	2.078 (4)
W···W′	3.4937 (8)		
S(1)–W–S(2)	132.68 (9)	S(2)–W–S(6)	82.52 (7)
S(1)–W–S(3)	50.76 (7)	S(3)–W–S(4)	135.50 (9)
S(1)–W–S(4)	86.06 (9)	S(3)–W–S(5)	100.3 (1)
S(1)–W–S(5)	104.0 (1)	S(3)–W–S(6)	80.28 (7)
S(1)–W–S(6)	127.63 (8)	S(4)–W–S(5)	100.4 (1)
S(2)–W–S(3)	153.05 (9)	S(4)–W–S(6)	132.36 (8)
S(2)–W–S(4)	51.4 (1)	S(5)–W–S(6)	101.7 (1)
S(2)–W–S(5)	103.4 (1)	W···S(6)···W′	90.5 (1)
S(1)–S(3)–W	63.84 (8)	S(2)–S(4)–W	63.7 (1)
S(3)–S(1)–W	65.40 (9)	S(4)–S(2)–W	64.9 (1)

[a] Estimated standard deviations in parentheses refer to the last significant digits.

in Table I. Bond distances and angles within the dianion are given in Table II. The anisotropic and isotropic thermal parameters for all atoms, the distances within the cation, the calculated hydrogen positions, the mean planes, and the observed and calculated structure factors are available as supplementary material.

Results and Discussion

The crystal structure of the complex consists of the dinuclear sulfide anion $W_2S_{11}^{2-}$ and tetraphenylphosphonium counterions. A view of the dianion with the atomic labeling scheme is shown in Figure 1. The coordination geometry about the W atom is best described as that of two pseudo pentagonal pyramids sharing a corner. The apical position of each pyramid is occupied by the terminal sulfido group S(5). The W atoms are each about 0.50 Å above the mean plane of the five basal sulfur atoms. The whole anion has a twofold axis passing through the S(6) atom, which relates the two pyramidal subunits in a syn geometry. The dihedral angle between the basal planes of the two moieties is around 49°, while the W–S(6)–W′ bridge angle is 90.5 (1)°. The skeletal geometry of this novel dianion is very similar to that of another W complex, $W_2S_{11}H^-$,[5] the most noticeable difference being the bridging ligand: a μ-η^3-S_2 ligand for $W_2S_{11}H^-$ with a terminal hydrogensulfido group and a μ-S ligand for $W_2S_{11}^{2-}$. The W–S–W bridge angle, the nonbonded W···W distance, the W–S(bridging) distances, and the dihedral angle between the two pyramidal groups in the two compounds are quite similar. Furthermore, $W_2S_{11}H^-$ can be derived from $W_2S_{11}^-$ by rotation of one pyramidal group around the apical axis leading to the replacement of μ-S by μ-η^3-S_2 as shown in Figure 2. Each W is coordinated by two η^2-S_2 groups; the S–S distances are in good agreement with the data usually reported for disulfido ligands.[6] The terminal metal–sulfido S(5) distance 2.070 (4) Å is very close to the corresponding W(VI)–S distances in the related compounds, i.e. $(PPh_4)_2W_3S_9$[7] and $(PPh_4)_2W_4S_{12}$.[8]

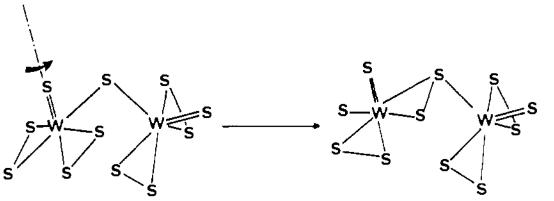

Figure 2. Structural relationship between the $W_2S_{11}^{2-}$ and $W_2S_{11}H^-$ anions.

The electronic absorption spectrum of $(PPh_4)_2W_2S_{11}$ in CH_3CN shows peaks at 470 and 370 nm and weak absorptions at ca. 550 and 340 nm. According to Müller et al.[6] CT transitions of type $\pi^*_v(S_2) \rightarrow d(\text{metal})$ should be located at ca. 500 nm. The absorption observed at 470 nm, consistent with the spectrum of $W_2S_{11}H^-$, which exhibits also a similar peak at 475 nm,[5] could be attributed to this CT transition. Another band is expected at higher energy related to the $\pi^*_h(S_2) \rightarrow d(\text{metal})$ transition; the peak observed at about 390 nm could be assigned to this transition.

The IR bands of $(PPh_4)_2W_2S_{11}$ in the range 600–250 cm^{-1}, 527 (vs), 492 (s), 452 (w), 345 (w), 320 (m), and 302 (w) cm^{-1}, are quite similar to those of $(PPh_4)_2W_2S_{11}H$, 527 (vs), 508 (s), 340 (w), 325 (w), and 309 (w) cm^{-1}, the main difference arising from the weak band at 452 cm^{-1} (bridging W–S–W vibration).[9] The three bands at about 320 cm^{-1} are attributed to the W–S stretching vibration of the W–S_2 unit. The absorptions observed at 527 and 492 cm^{-1} are respectively characteristic of the PPh_4^+ cation and of the terminal W═S vibration. Other bands associated with the S_2^{2-} groups are expected between 480 and 565 cm^{-1}[6] but not assigned in the spectra.

Supplementary Material Available: Listings of cation bond lengths and angles, mean planes, anisotropic thermal parameters for non-hydrogen atoms, and calculated position parameters for H atoms and an ORTEP stereoview for the anion (5 pages); a listing of observed and calculated structure factors (15 pages). Ordering information is given on any current masthead page.

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