mixed-valence of Ni(II)–Ni(IV) system.[3] However again, the corresponding bromide salt did not give a resonance Raman spectrum.

In a future paper we will describe the conductivity properties of this material.

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Registry No. [Ni(chxn)$_2$]Br$_2$, 92621-07-3; [Ni(chxn)$_3$]Br$_2$, 92621-08-4; Br$_2$, 7726-95-6.

Supplementary Material Available: A listing of observed and calculated structure factors, Figure 5, showing a graph of the Patterson function along the *w* coordinate around the point $(u, v, w) = (0, 0, 0.5)$, and lists of anisotropic thermal parameters, *R* factors, and bond distances and angles (15 pages). Ordering information is given on any current masthead page.

Contribution from the Corporate Research Science Laboratory, Exxon Research and Engineering Company, Annandale, New Jersey 08801, and Department of Chemistry, University of Arizona, Tucson, Arizona 85721

Reactions of Tetrathiometalates, MS_4^{2-} (M = Mo, W). Syntheses and Properties of $M_2S_4^{2+}$-Containing Compounds. Structure of Bis(tetraphenylphosphonium) Bis(μ-sulfido)bis(sulfido(1,2-ethanedithiolato)tungstate(V)), $[P(C_6H_5)_4]_2[W_2S_4(S_2C_2H_4)_2]$

WIE-HIN PAN,[†] TRAVIS CHANDLER,[‡] JOHN H. ENEMARK,[‡] and EDWARD I. STIEFEL*[†]

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Heating ammonium salts of MS_4^{2-} (M = Mo, W) in DMF for 1–3 h in the presence of either 1,2-ethanedithiol or *o*-aminobenzenethiol (LH$_2$) provides a convenient route to $M_2S_4L_2^{2-}$ compounds. The W and Mo compounds have similar spectroscopic and structural properties. The complex $[P(C_6H_5)_4]_2[W_2S_4(1,2\text{-ethanedithiolate})_2]$ crystallizes in the monoclinic crystal system, space group $P2_1/n$, with unit cell dimensions $a = 16.126$ (7) Å, $b = 25.03$ (1) Å, $c = 13.021$ (6) Å, and $\beta = 101.73$ (4)° and a unit cell volume of 5145 (4) Å^3. The dinuclear complex contains a *syn*-$W_2S_4^{2+}$ core. The W–W distance of 2.86 Å is identical with that in the Mo analogue but is 0.05 Å shorter than the corresponding distance in $W_2S_4(WS_4)_2^{2-}$. It is possible that internal redox is involved in the formation of $M_2S_4^{2+}$ cores.

The binary tetrathiometalate anions, MS_4^{2-} (M = Mo, W), have been known for almost 100 years.[1] Until recently, studies on these anions were carried out mainly in aqueous solvents at ambient temperatures.[1,2] In nonaqueous solvents and at moderately elevated temperatures MS_4^{2-} undergoes interesting thermal reactions.[3] Studies of these reactions may lead to insight regarding the mechanism of thermal conversion of MS_4^{2-} to MS_3 and ultimately to MS_2.[4] In *N,N*-dimethylformamide, at 90 °C, $(NH_4)_2MoS_4$ gives the stable molecular ion $Mo_3S_9^{2-}$ (i.e., $(MoS_3)_3^{2-}$),[3] which may be an intermediate in the formation of MoS_3 from MoS_4^{2-}.

The formation of $M_3S_9^{2-}$ from MS_4^{2-} probably involves an internal redox reaction where coordinated S^{2-} is the reducing agent. However, in the presence of external reducing agents such as 1,2-ethanedithiol (edtH$_2$) or *o*-aminobenzenethiol (abtH$_2$), a product containing the $M_2S_4^{2+}$ core is obtained. This reaction is of considerable synthetic interest. Previously, $Mo_2S_4^{2+}$ compounds had been prepared in high yield starting from $Mo_2(S_2)_6^{2-}$.[5] However, the tungsten analogue, $W_2(S_2)_6^{2-}$, has not been prepared, thereby precluding the preparation of $W_2S_4^{2+}$ species via this route. This is unfortunate since heretofore examples of compounds containing the $W_2S_4^{2+}$ core are limited to two, namely $W_4S_{12}^{2-}$[6] and $W_2S_4(S_2PR_2)_2$.[7] Of these two, only the structure of the tetranuclear ion, $W_4S_{12}^{2-}$, has been confirmed.[6]

In this report, we describe a convenient route to preparing $M_2S_4^{2+}$-containing compounds using MS_4^{2-} as the starting material. We also confirm the formation of compounds containing the $W_2S_4^{2+}$ core by reporting the full crystal structure determination of $[P(C_6H_5)_4]_2W_2S_4(edt)_2$.

Experimental Section

Syntheses. Solvents, *N,N*-dimethylformamide (DMF) and acetonitrile, were obtained from Burdick & Jackson. DMF was distilled once before use, and CH$_3$CN was refluxed over CaH$_2$ and then distilled before use. The thiols, 1,2-ethanedithiol (edtH$_2$) and *o*-aminobenzenethiol (abtH$_2$), were used as received from Aldrich Chemical Co. $(NH_4)_2WS_4$ and $(NH_4)_2MoS_4$ were prepared as previously described.[3] Elemental analyses were performed by Galbraith Laboratories and the Analytical and Information Division of Exxon Research and Engineering Co.

$[N(C_2H_5)_4]_2Mo_2S_4(edt)_2$. A degassed solution of edtH$_2$ (0.63 mL, 7.5 mmol) in 32 mL of DMF was added to $(NH_4)_2MoS_4$ (1.26 g, 4.9 mmol) under an atmosphere of N$_2$. The resulting solution was stirred and heated at 90 °C for 60 min. After the solution was cooled to room temperature, $[N(C_2H_5)_4]Br$ (1.5 g) was added and allowed to dissolve. The reaction mixture was filtered, and diethyl ether was added to the filtrate to the point of incipient precipitation. When the filtrate was allowed to stand and cool, (~−20 °C), orange-red

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[†] Exxon Research and Engineering Co.

[‡] University of Arizona.

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crystals formed. The crystals were filtered, washed with diethyl ether, and air-dried. Yield: 1.2 g (63%). Anal. Calcd for $C_{20}H_{40}N_2Mo_2S_8$: C, 31.4; H, 6.3; N, 3.7. Found: C, 31.1; H, 6.6; N, 4.1.

$[N(C_2H_5)_4]_2Mo_2S_4(abt)_2$. A DMF solution (25 mL) of a mixture of $(NH_4)_2MoS_4$ (1.45 g, 5.6 mmol) and $abtH_2$ (1.5 mL, 14.1 mmol) was stirred under N_2 while being heated at 95 °C. After about 45 min, the reaction solution was deep red-orange and its UV–vis spectrum indicated that most of the MoS_4^{2-} had reacted. After the solution was cooled to room temperature, $[N(C_2H_5)_4]Br$ (2.35 g) was added and allowed to dissolve. The resulting solution was then chromatographed on 200 mL of activity V neutral alumina (Fisher; ca. 15% water content) with CH_3CN as eluant. A major dark red band, which eluted first, was collected. The volume of this fraction was reduced by half, and 50 mL of CH_3OH and 25 mL of diethyl ether were added, giving a red-brown precipitate. After cooling ($\sim$−20 °C) (ca. 2 h), the red-brown precipitate was filtered, washed with diethyl ether, and air-dried. Although the IR and UV–vis spectra of this precipitate appeared consistent with $[N(C_2H_5)_4]_2Mo_2S_4(abt)_2$, the elemental analysis indicated it to be impure. Thus, the solid was redissolved in CH_3CN and rechromatographed on activity V neutral alumina. A brown band remained stationary at the top of the column while a red band eluted with the CH_3CN. The fraction from the red band was collected, and its volume reduced to one-tenth, producing a red-brown precipitate. This red-brown solid was the pure product. Anal. Calcd for $C_{28}H_{50}N_4Mo_2S_6$: C, 40.7; H, 6.1; N, 6.8. Found: C, 40.6; H, 6.2; N, 6.8.

$[N(C_2H_5)_4]_2W_2S_4(edt)_2$. $(NH_4)_2WS_4$ (0.81 g, 2.3 mmol) dissolved in 15 mL of degassed DMF was added to a solution of 1,2-ethanedithiol (0.3 mL, 3.6 mmol) in 10 mL of DMF. The resulting solution was heated to 145 °C for ca. 2 h. After the solution was cooled to room temperature, $[N(C_2H_5)_4]Br$ (0.8 g) was added to the orange-red solution. Addition of diethyl ether precipitated the product as orange-red crystals that were mixed with a white solid. The precipitate was filtered and washed with methanol, which dissolved the white solid. Addition of more ether to the filtrate precipitated more product. Total yield of orange-red crystals was 0.61 g (55%). Anal. calcd for $C_{20}H_{48}N_2W_2S_8$: C, 25.5; H, 5.1; N, 3.0. Found: C, 25.7; H, 5.3; N, 3.1. The tetraphenylphosphonium salt was similarly prepared by using $[P(C_6H_5)_4]Br$ in place of $[N(C_2H_5)_4]Br$.

$[N(C_2H_5)_4]_2W_2S_4(abt)_2$. *o*-Aminobenzenethiol ($abtH_2$) (0.3 mL, 2.8 mmol) in 5 mL of DMF was added to a 5-mL DMF solution of $(NH_4)_2WS_4$ (0.28 g, 0.81 mmol). The yellow solution was stirred and heated ($\sim$130 °C) under argon and gradually turned orange-red. After 2 h, the UV–vis spectrum of the reaction solution indicated that all the WS_4^{2-} had reacted. $[N(C_2H_5)_4]Br$ (0.4 g) was added to the reaction solution after it was cooled to room temperature. Diethyl ether was slowly added until the solution became cloudy. After the mixture was cooled in the refrigerator (ca. 6 °C) for 1 h, the red-orange precipitate was filtered off, washed with a mixture of methanol/diethyl ether, and air-dried. Yield: 0.33 g (81%). Anal. Calcd for $C_{28}H_{50}N_4W_2S_6$ $[N(C_2H_5)_4)_2W_2S_4(abt)_2]$: C, 33.5; H, 5.0; N, 5.6. Found C, 34.1; H, 5.2; N, 5.6.

Physical Measurements. Infrared spectra of the samples as KBr pellets were obtained on a Perkin-Elmer Model 683 IR spectrophotometer. UV–vis spectra were obtained in CH_3CN solutions on a Perkin-Elmer Model 330 spectrophotometer.

X-ray Crystallography of $[P(C_6H_5)_4]_2W_2S_4(edt)_2$. Crystals of $[P(C_6H_5)_4]_2W_2S_4(edt)_2$ were obtained from CH_3CN/Et_2O solution. A representative multifaceted crystal was mounted on a glass fiber with epoxy cement. A rotation photograph and subsequent ω scans of three reflections showed that the mosaicity of the crystal was satisfactory.

Unit cell parameters were determined by least-squares refinement of the setting angles of 15 reflections that were centered automatically on a Syntex P2$_1$ four-circle diffractometer. Axial photographs verified the selection of a monoclinic lattice. Data were collected by using the θ–2θ scan mode. Details of data collection are listed in Table I. No systematic variations of the check reflections occurred during data collection.

The intensities were corrected for polarization and Lorentz effects. The space group $P2_1/n$ was selected on the basis of systematic absences ($h0l$, $h + l \neq 2n$; $0k0$, $k \neq 2n$). This nonstandard space group has equivalent positions $\pm(x, y, z)$ and $\pm(x + {}^1/_2, {}^1/_2 - y, z + {}^1/_2)$. The unit cell volume and density indicated one dimer per asymmetric unit.

The structure was solved by using the 4291 data with $2\theta < 40.0°$ and having $F_o^2 > 3\sigma(F_o^2)$. The positions of the tungsten atoms were determined from the Patterson function. Refinement of these atoms resulted in $R = 0.42$ and $R_w = 0.49$, where $R = \sum(||F_o| - |F_c||)/\sum|F_o|$ and $R_w = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2}$. Other non-hydrogen atoms were located by a series of structure factor calculations and difference electron density maps (FORDAP).[8] Full-matrix least-squares refinement of the structure was based on F_o, with the quantity $\sum w(|F_o| - |F_c|)^2$ being minimized (NUCLS).[8] The weights were taken as $w = 4F_o^2/\sigma^2(F_o^2)$.

Table I. Crystal Data for $[PPh_4]_2W_2S_4(edt)_2$

mol formula	$W_2S_8P_2C_{52}H_{48}$
mol wt	1359.07
cryst color, habit	red, multifaceted
cryst dimens, mm	0.4 × 0.4 × 0.6
μ, cm^{-1}	50.5
radiation wavelength, Å	0.7107 (Mo Kα)
space group	$P2_1/n$
a, Å	16.126 (7)
b, Å	25.03 (1)
c, Å	13.021 (6)
β, deg	101.73 (4)
unit cell vol, Å^3	5145 (4)
Z	4
density calcd, g cm^{-3}	1.755
density obsd,[a] g cm^{-3}	1.757
scan mode	θ–2θ
scan range, 2θ, deg	2.0–50.0
scan rate, deg/min	2.02–29.3
no. of check reflcns/data	3/97
no. of unique data	9793
no. of data with $F_o^2/3\sigma(F_o^2)$	7414
no. of variables	201
final R	0.039
final R_w	0.046
σ for observn of unit wt	1.80

[a] By flotation in $C_7H_{16}/CHBr_2CHBr_2$.

Scattering factors for neutral atoms were from Cromer and Waber for tungsten[9] and from Doyle and Turner for sulfur, phosphorus, and carbon.[9] Hydrogen scattering factors were from Cromer and Mann.[9] Anomalous scattering factors for tungsten, sulfur, and phosphorus were from Cromer and Liberman.[9] The 48 carbon atoms in the phenyl groups were refined isotropically as rigid groups (D_{6h} symmetry; C–C = 1.383 Å). Further refinement of all non-hydrogen atoms, with anisotropic temperature factors for the tungsten atoms, using the 7414 data with $2\theta < 50.0°$ and $F_o^2 > 3\sigma(F_o^2)$ resulted in $R = 0.065$ and $R_w = 0.078$.

An empirical absorption correction using the program TAPER.[10] was made on the intensities. The absorption profiles were obtained for 15 reflections ranging in 2θ from 6.69 to 48.51°. Absorption profile data were collected at 10° intervals of ψ over 360°. The largest variation in intensity, ca. 40%, occurred for the reflection at low 2θ (6.69°). Two additional cycles of refinement, with anisotropic temperature factors for all nongroup atoms, using the absorbance-corrected data gave $R_w = 0.062$. At this point the positions of the 48 hydrogen atoms of the structure were calculated with C–H bond distances of 1.073 Å for methylene hydrogens and 1.085 Å for the phenyl hydrogens. These atoms were included as fixed contributions to the structure factors. Refinement converged with $R = 0.039$, $R_w = 0.046$, and a "goodness of fit" $[\sum w(|F_o| - |F_c|)^2/(n - m)]^{1/2} = 1.80$, where n is the number of reflections used in the refinement and m is the number of variables. The largest residual peak (0.88 e/Å^3) in the final difference map was located 1.09 Å from W2 on the W1–W2 internuclear axis.

Results

Syntheses. The compounds $M_2S_4(edt)_2^{2-}$ and $M_2S_4(abt)_2^{2-}$ (M = Mo, W) are obtained in relatively high yields from the reactions of $(NH_4)_2MS_4$ with $edtH_2$ or $abtH_2$, respectively. The conditions used (DMF as solvent, at 90 °C for M = Mo

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(8) Computer programs used were local modifications of Zalkin's FORDAP, Ibers' NUCLS, Busing and Levy's ORFFE, and Johnson's ORTEP.

(9) Ibers, J. A.; Hamilton, W. C. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, Tables 2.2A and 2.3.1.

(10) TAPER is a data processing program supplied by Syntex Analytical Instruments with the P2$_1$ Fortran X-ray diffractometer system.

Table II. Infrared and Electronic Spectroscopic Data

compd	IR:[a] ν, cm^{-1}	UV-vis:[b] λ, nm ($10^{-3}\epsilon$, M^{-1} cm^{-1})
$[N(C_2H_5)_4]_2$-$Mo_2S_4(edt)_2$	517 (s), 466 (w), 436 (w), 415 (w), 345 (w), 327 (s), 294 (w)	448 (2.14), 308 (7.15)
$[N(C_2H_5)_4]_2$-$Mo_2S_4(abt)_2$	510 (vs), 455 (m), 455 (m), 385 (w), 345 (w)	525 (sh, 4.0), 370 (25.0), 325 (31.0), 300 (sh, 29.0)
$[N(C_2H_5)_4]_2$-$W_2S_4(edt)_2$	504 (vs), 465 (w), 428 (w), 342 (w), 325 (s), 296 (w)	382 (8.3), 284 (29.0)
$[N(C_2H_5)_4]_2$-$W_2S_4(abt)_2$	500 (vs), 455 (s), 440 (m), 395 (w), 345 (w)	420 (sh, 4.2), 310 (37.0), 290 (32.0)

[a] KBr pellets. [b] CH_3CN solutions.

Table III. Final Positional Parameters for the Anion $W_2S_4(edt)_2^{2-}$ and the Two P Atoms of the Cations

atom	x	y	z
W1	0.07169 (2)	0.18985 (1)	0.08240 (2)
W2	0.08496 (2)	0.30322 (1)	0.10964 (2)
S1	−0.0602 (1)	0.17621 (9)	0.0204 (2)
S2	−0.0421 (1)	0.33232 (9)	0.0621 (2)
S3	−0.3747 (1)	0.24803 (7)	0.4798 (1)
S4	0.0805 (1)	0.23815 (8)	0.2371 (1)
S5	0.1258 (1)	0.12441 (8)	0.2154 (2)
S6	−0.3609 (1)	0.36829 (9)	0.4781 (2)
S7	0.1557 (1)	0.34597 (8)	0.2674 (2)
S8	0.1635 (1)	0.36909 (8)	0.0331 (2)
P1	−0.1383 (1)	0.48380 (7)	0.2716 (1)
P2	−0.5091 (1)	0.32497 (7)	0.1147 (1)
C5	0.1701 (6)	0.0694 (4)	0.1535 (8)
C6	0.1303 (7)	0.0680 (4)	0.0785 (8)
C7	0.2057 (5)	0.4074 (3)	0.2261 (7)
C8	0.1646 (6)	0.4249 (3)	0.1232 (7)

Table IV[a]

Bond Distances (Å) and Esd's for the Anion $W_2S_4(edt)_2^{2-}$

W1-W2	2.862 (1)		
W1-S1	2.143 (2) (2.156 (2))	W2-S2	2.144 (2) (2.154 (2))
W1-S3	2.328 (2)	W2-S3	2.319 (2)
W1-S4	2.328 (2)	W2-S4	2.336 (2)
W1-S5	2.414 (2)	W2-S7	2.391 (2)
W1-S6	2.397 (2)	W2-S8	2.415 (2)
S5-C5	1.814 (10)	S7-C7	1.835 (9)
S6-C6	1.819 (10)	S8-C8	1.822 (9)
C5-C6	1.51 (1)	C7-C8	1.51 (1)

Bond Angles (deg) and Esd's for the Anion $W_2S_4(edt)_2^{2-}$

S1-W1-W2	104.36 (6)	S2-W2-W1	104.96 (6)
S1-W1-S3	110.28 (8)	S2-W2-S3	111.78 (8)
S1-W1-S4	106.85 (8)	S2-W2-S4	106.05 (8)
S1-W1-S5	110.37 (9)	S2-W2-S7	110.92 (8)
S1-W1-S6	102.69 (9)	S2-W2-S8	101.52 (8)
S3-W1-S4	100.66 (7)	S3-W2-S4	100.71 (7)
W1-S3-W2	76.04 (6)		
W1-S4-W2	75.70 (6)		
S3-W1-S5	137.94 (8)	S3-W2-S7	135.95 (8)
S4-W1-S6	148.25 (8)	S4-W2-S8	149.71 (8)
S3-W1-S6	79.41 (8)	S3-W2-S8	80.10 (7)
S4-W1-S5	77.43 (8)	S4-W2-S7	77.28 (7)
S5-W1-S6	81.66 (8)	S7-W2-S8	81.40 (8)
W1-S5-C5	108.3 (4)	W2-S7-C7	108.6 (4)
W1-S6-C6	102.5 (4)	W2-S8-C8	101.2 (4)
S5-C5-C6	110.4 (7)	S7-C7-C8	110.2 (6)
S6--C6-C5	109.4 (7)	S8-C8-C7	109.3 (6)

Dihedral Angle (deg) between Tungsten and Bridging Sulfur Planes

W1-S3-S4/W2-S3-S4	148.9 (1)

[a] The bond distances in parentheses were averaged over the thermal motions of the atoms, with the second atom assumed to ride on the first. The angles, distances and errors for the anion were calculated by the program ORFFE.[8]

Table V. Least-Squares Planes in the $W_2S_4(edt)_2^{2-}$ Anion[a]

Plane I: $-0.9271x - 0.1419y - 0.3470z + 2.6241 = 0.0$

S3	−0.105 (2)	S6	0.120 (2)
S4	0.107 (2)	W1	0.716
S5	−0.122 (2)		

Plane II: $-0.9108x + 0.3095y - 0.2734z - 0.2670 = 0.0$

S3	−0.134 (2)	S8	0.155 (2)
S4	0.140 (2)	W2	0.716
S7	−0.161 (2)		

[a] Rms deviations of the fitted atoms from the planes are 0.114 Å for the plane I and 0.148 Å for plane II. Equations were fitted to the sulfur atom coordinates.

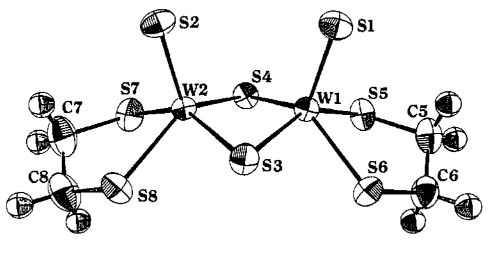

Figure 1. ORTEP drawing of the anion $W_2S_4(edt)_2^{2-}$ with thermal ellipsoids showing 50% electron probability distribution.

and 140 °C for M = W) were identical with those used for preparing[3] $Mo_3S_9^{2-}$ and $W_3S_9^{2-}$ from $(NH_4)_2MoS_4$ and $(NH_4)_2WS_4$, respectively. However, while $M_3S_9^{2-}$ complexes failed to form in CH_3CN, we have succeeded in preparing $[P(C_6H_5)_4]_2W_2S_4(edt)_2$ and $[N(C_2H_5)_4]_2W_2S_4(abt)_2$ in refluxing CH_3CN solutions. The two $W_2S_4L_4$ products prepared in CH_3CN were identified by IR spectroscopy. The former was prepared by reacting $(NH_4)_2WS_4$ with $[N(C_2H_5)_3H]_2$edt, and the latter by reacting $(NH_4)_2WS_4$ with abtH_2. In both reactions, some $(NH_4)_2WS_4$ remained unreacted after more than 3 h. $(NH_4)_2MoS_4$ also reacted with abtH_2 in CH_3CN under reflux at 95 °C, yielding $Mo_2S_4(abt)_2^{2-}$. However, under similar conditions $[N(C_2H_5)_4]MoS_4$ did not react with edtH_2.

Attempted reaction of $Mo_3S_9^{2-}$ with edtH_2 in DMF did not form $Mo_2S_4(edt)_2^{2-}$, indicating that $Mo_3S_9^{2-}$ is not an intermediate in the formation of the $Mo_2S_4^{2+}$ complexes. In light of the recent report of the formation[11a] of $Mo_2S_8^{2-}$ from the reaction of MoS_4^{2-} with diphenyl disulfide, it occurred to us that an oxidized form of 1,2-ethanedithiol, a potential contaminant in the edtH_2 used, could react with MoS_4^{2-} to form $Mo_2S_8^{2-}$, an intermediate that could subsequently react with edtH_2 to give $Mo_2S_4(edt)_2^{2-}$. This possibility was rendered unlikely by the finding that, after the edtH_2 was purified by vacuum distillation, the reaction with $(NH_4)_2MoS_4$ still proceeded smoothly to give a 70% yield of $Mo_2S_4(edt)_2^{2-}$. Although the formation of $M_2S_4^{2+}$ species from MS_4^{2-} occurs in reactions with edtH_2 and abtH_2, the dithiols bis(mercaptoethyl) ether $[HS(CH_2)_2O(CH_2)_2SH]$ and bis(mercaptoethyl)) sulfide $[HS(CH_2)_2S(CH_2)_2SH]$ lead only to the formation of $Mo_3S_9^{2-}$ upon reaction with $(NH_4)_2MoS_4$ in DMF.[3] In related studies, Coucouvanis and co-workers have prepared sulfur-rich $Mo_2S_4^{2+}$-core complexes from MoS_4^{2-} and either elemental sulfur or organic trisulfides.[11b]

IR and UV-Vis Spectra. Spectroscopic data for the four compounds reported here are summarized in Table II. Except for the small shifts in peak positions, the IR spectra of $W_2S_4(edt)_2^{2-}$ and $Mo_2S_4(edt)_2^{2-}$ are practically identical.

Structure of $[P(C_6H_5)_4]_2W_2S_4(edt)_2$. Final positional parameters for the atoms are listed in Table III. Bond angles and distances with standard errors are listed in Table IV.

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Derived parameters for atoms refined as rigid groups and tables of observed and calculated structure factors are available as supplementary material.

An ORTEP[8] drawing of the dianion is shown in Figure 1. The structure consists of a $W_2S_4^{2+}$ unit in the syn isomeric form. Each tungsten atom is surrounded by five sulfur atoms in a distorted square-pyramidal arrangement, where two of the sulfurs are shared by the two W atoms. The W atoms are each 0.72 Å above the least-squares planes of the four basal sulfur atoms in each distorted square-pyramidal unit (see Table V).

Despite the similarity of the halves of the dianion, strict C_{2v} symmetry is not observed. If the W_2S_2 ring is used as a frame of reference, the most noticeable deviation is the inclination of both terminal sulfido atoms toward the S5, S4, S7 side of the anion. In this "cis" distortion, S5 and S7 rotate away from the terminal sulfido atoms while S6 and S8 move toward them (see Table IV). The resultant S4–W1–S6 and S4–W2–S8 angles are more than 10° larger than the corresponding S3–W1–S5 and S3–W2–S7 angles. This distortion toward a trigonal-bipyramidal configuration at each tungsten atom reduces the overall symmetry of the dianion to C_s. These distortions also can be seen in the large deviations of the basal sulfur atoms from their least-squares plane (see Table V).

The 1,2-ethanedithiolate carbon atoms are well-behaved with reasonable bonding distances and no evidence for disorder. This is in contrast to *syn*-$Mo_2S_4(edt)_2^{2-}$[12] where the C–C bond lengths were unrealistically short due to disorder.

The tetraphenylphosphonium cations have an average P–C bond distance of 1.806 (7) Å and an average C–P–C bond angle of 109 (1)°. The ordered cations and the well-behaved 1,2-ethanedithiolato ligands enabled the structural parameters to be determined with greater precision than those for *syn*-$[N(C_2H_5)_4]_2Mo_2S_4(edt)_2$. In the latter case, disorder of the $[N(C_2H_5)_4]^+$ cations and large thermal parameters prevented precise determination of the parameters of several light atoms in both the anion and the cation.[12] Our attempts to crystallize $[N(C_2H_5)_4]_2W_2S_4(edt)_2$ failed to produce satisfactory crystals for an X-ray structure determination.

Discussion

Reactions of MS_4^{2-}. Although the reactions of MoS_4^{2-} with $edtH_2$ and $abtH_2$ did not produce new compounds, the corresponding reactions with WS_4^{2-} led to a much needed synthetic route to new $W_2S_4^{2+}$ species. The only other $W_2S_4^{2+}$ compounds reported in the literature, $W_4S_{12}^{2-}$ and $W_2S_4(S_2PR_2)_2$, were prepared by different methods. $W_4S_{12}^{2-}$ was prepared[6] from the reaction of WS_4^{2-} with acetic acid in CH_2Cl_2 while $W_2S_4(S_2PR_2)_2$ was prepared[7] by reacting $W(CO)_6$ with the disulfide $(S_2PR_2)_2$. The first example of the related $W_2O_2S_2^{2+}$ compound $W_2O_2(\mu\text{-}S)_2Cl_4^{2-}$ was recently reported[13] by Drew et al. The compound was obtained from a mixture of $WOSCl_2$ and $(AsPh_4)Cl$ in CH_2Cl_2 in the presence of air.

In the present reactions the starting hexavalent WS_4^{2-} ion is reduced to form dinuclear pentavalent W complexes. The reductant could be either the $edtH_2$ or $abtH_2$ ligand or the sulfide already present in the W coordination sphere. If S^{2-} is the reductant, the mechanism of reduction may be akin to that proposed[3] for the formation of M_3S_9 (M = Mo, W), involving internal electron transfer from sulfide to M. Such internal electron transfers may be common features of M–S coordination chemistry[11] and can sometimes be induced by external redox agents.[11,14] Additional kinetic and reaction studies are under way to probe mechanistic features of these and related reactions.

Table VI. Comparison of Average Distances and Angles in $M_2S_4^{2+}$-Containing Compounds[a]

	I[b]	II[b]	III[b]
	Distances (Å)		
M-M	2.862 (1)	2.912 (6)	2.863 (2)
M-S(t)	2.144 (2)	2.089 (19)	2.101 (4)
M-S(b)	2.328 (2)	2.333 (20)	2.320 (3)
M-S1	2.404 (2)	2.487 (22)	2.406 (3)
	Angles (deg)		
M-S(b)-M	75.9 (6)	77.2 (6)	76.23 (9)
S(b)-M-S(b)	100.69 (7)	98.7 (6)	98.9 (1)
dihed angle[c]	148.9 (1)	147.5	146.9 (1)

[a] Standard deviations are in parentheses. Where several measurements were averaged, the standard deviation provided is the largest deviation of the several values. [b] I = $W_2S_4(edt)_2^{2-}$; this work. II = $W_4S_{12}^{2-}$; ref 6. III = $Mo_2S_4(edt)_2^{2-}$; ref 12. [c] Each plane of the dihedral angle is defined by the bridging sulfur atoms and one metal atom: S(b)-M1-S(b)/S(b)-M2-S(b).

Structure of $W_2S_4(edt)_2^{2-}$. Other than the slight trigonal-bipyramidal distortions at each W, the structure of $W_2S_4(edt)_2^{2-}$ is very similar to that of $Mo_2S_4(edt)_2^{2-}$.[12] The short W1–W2 distance (2.862 (1) Å) is comparable to that in $W_2O_2(\mu\text{-}S)_2Cl_4^{2-}$[13] and can be interpreted in terms of a metal–metal σ bond formed from the overlap of W $5d_{x^2-y^2}$ orbitals.[15] A similar short Mo–Mo distance is also observed in $Mo_2S_4(edt)_2^{2-}$ (see Table VI). One of the two unique anions in the structure of $[PPh_4]_2W_4S_{12}$[6] has a "trans" distortion, with the terminal sulfido ligands twisted toward opposite sides of the anion. The other $W_4S_{12}^{2-}$ anion in the asymmetric unit shows smaller irregular distortions. All of these distortions are probably due to lattice effects and may indicate a fair amount of flexibility in the anions.

The central W–W bond in $W_4S_{12}^{2-}$ is longer than the W–W bond in $W_2S_4(edt)_2^{2-}$ by about 0.05 Å (Table VI). In $W_4S_{12}^{2-}$, the 5d orbitals on the external W atoms overlap the internal W–W bonding orbital, removing electron density and weakening the interaction between the two internal W atoms. The interaction of the W atoms in $W_4S_{12}^{2-}$ can be considered as a four-center, two-electron bond, composed of the totally symmetric combination of four $5d_{x^2-y^2}$ orbitals (a′ symmetry). Because the external W–internal W distances are longer than the internal W–internal W distance, it is likely that the electron density remains largely on the two internal W atoms and the contribution of the external W atoms to the bond is relatively small. Nevertheless, the difference of 0.05 Å in the metal–metal bond distances of $W_4S_{12}^{2-}$ and $W_2S_4(edt)_2^{2-}$ provides strong evidence of the ability of MS_4^{2-} ligands to accept electron density. This ability has been noted previously in $M_3S_9^{2-}$,[3] $Fe(MS_4)_2^{3-}$,[19] and similar complexes.[20] The pair of electrons on the central metal atom of $M_3S_9^{2-}$ compounds is

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expected to be more available than the metal–metal bonding pair in the $M_2S_4^{2+}$ core. The difference of 0.13 Å in the average distances of the external W–internal W atoms for $W_3S_9^{2-}$ (2.95 Å)[3] and $W_4S_{12}^{2-}$ (3.08 Å)[6] can be understood in terms of the greater facility with which MS_4^{2-} can act as an electron acceptor in the trinuclear than in the tetranuclear complex.

The average W–S(t) bond distance in $W_2S_4(edt)_2^{2-}$ is longer than the corresponding distances for either $W_4S_{12}^{2-}$ or $Mo_2S_4(edt)_2^{2-}$ by 0.05 and 0.04 Å, respectively (see Table VI). For $W_4S_{12}^{2-}$ the difference may be a consequence of the four-center bond, where removal of electron density from the internal W atoms would reduce repulsion of the terminal sulfido atoms. A related effect may be occurring in the $Mo_2S_4(edt)_2^{2-}$ case, where there are 32 fewer electrons in the molybdenum core. Additional tungsten core electrons repel multiply bonded atoms in quadruply bonded tungsten,[16] and this effect could apply to π-bonded terminal sulfido atoms. The distances of the Mo–S(t) bonds in other Mo(V) dimers[18] ligated exclusively by sulfur are shorter than the W–S(t) distances in $W_2S_4(edt)_2^{2-}$, consistent with this idea.

An alternative explanation for this difference in the M–S(t) bond lengths of these complexes is the partial occupancy of the sulfido coordination site by oxo ligands,[12] caused by partial hydrolysis of the terminal sulfido atoms. An extreme example of such a disorder was observed for $W_3S_9^{2-}$.[17] Smaller amounts of oxo contamination that are not accounted for during structure refinement would result in an artificially short determination of the M–S(t) bond length.[18a] The unavailability of infrared spectroscopic data on the samples on which the structures have been determined makes it impossible to gauge the presence or magnitude of this effect. However, in the present case, the longer W–S(t) bond makes the presence of oxo impurities very unlikely.

Conclusion

The thermal reactions of $(NH_4)_2MS_4$ (M = Mo, W) with $edtH_2$ or $abtH_2$ yield $M_2S_4^{2+}$-containing species. The reduction of M^{VI} in MS_4^{2-} to M^V may take place by internal redox rather than by reduction by the added thiols in a reaction path that does not involve $M_3S_9^{2-}$ as an intermediate. The structure of $[P(C_6H_5)_4]_2W_2S_4(edt)_2$ reveals a *syn*-$W_2S_4^{2+}$ core with dimensions very similar to those of the Mo analogue. This is the first structurally confirmed $W_2S_4^{2+}$ core in a dinuclear complex.

Registry No. $[N(C_2H_5)_4]_2Mo_2S_4(edt)_2$, 92763-40-1; $[N(C_2H_5)_4]_2Mo_2S_4(abt)_2$, 84056-94-0; $[N(C_2H_5)_4]_2W_2S_4(edt)_2$, 84051-18-3; $[N(C_2H_5)_4]_2W_2S_4(abt)_2$, 84056-96-2; $(NH_4)_2MoS_4$, 13106-76-8; $(NH_4)_2WS_4$, 13862-78-7; $[P(C_6H_5)_4]_2W_2S_4(edt)_2$, 92843-00-0.

Supplementary Material Available: Listings of calculated and observed structure factors, anisotropic thermal parameters, and derived parameters for atoms in rigid groups (35 pages). Ordering information is given on any current masthead page.

Contribution from the Anorganisch Chemisch Laboratorium, University of Amsterdam, 1018 WV Amsterdam, The Netherlands, and Laboratoire d'Applications, Bruker Spectrospin, 67106 Wissembourg, France

^{1}H and INEPT ^{15}N and ^{109}Ag NMR Studies of the Structural and Dynamic Features in Solution of Some Silver(I) and Copper(I) Complexes with Polydentate N_4-Donor Ligands, (*R*,*S*)-1,2-(6-R-py-2-CH=N)$_2$Cy and 1,2-(6-R-py-2-CH=N)$_2$Et (Cy = Cyclohexane, Et = Ethane, R = H or Me)

GERARD C. VAN STEIN,[†] GERARD VAN KOTEN,*[†] KEES VRIEZE,[†] and CHRISTIAN BREVARD[‡]

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The reactions of the neutral N_4-donor ligand system 1,2-(6-R-py-2-CH=N)$_2$Et (R = H or Me) with $[M(O_3SCF_3)]$ (M = Ag(I) or Cu(I)) yielded ionic complexes, consisting of a $[M_2(N_4)_2]^{2+}$ dication and $O_3SCF_3^-$ anions, which have been characterized by field-desorption mass spectrometry and INEPT ^{15}N and ^{109}Ag NMR. The dynamic behavior in solution of these $[M_2(N_4)_2]^{2+}$ dications as well as of the analogous dications with the N_4 ligands (*R*,*S*)-1,2-(6-R-py-2-CH=N)$_2$Cy (Cy = cyclohexane, R = H or Me) has been studied by ^{1}H NMR. The $[M_2(N_4)_2]^{2+}$ dications have a twofold axial symmetry. The N_4 ligands coordinate to the metal 1B centers as bis-bidentates. The metal 1B centers in the dications have similar configurations ($\Delta\Delta$ or $\Lambda\Lambda$). Because of the presence of two inequivalent pyridine–imine H sites in these dications and the presence of $^3J(^1H-^{107,109}Ag)$ in the ^{1}H NMR spectra of the silver(I) complexes, intra- and intermolecular exchange processes could be studied in solution by ^{1}H NMR. In the spectra of the metal 1B complexes with the ethanediyl bridges a fast conformational movement was observed between two identical structures. In contrast this conformational movement does not occur in the complexes with the (*R*,*S*)-cyclohexanediyl bridging groups. The silver(I) complexes are prone to intermolecular Ag^+ exchange, which occurs with loss of $^3J(^1H-^{107,109}Ag)$. This intermolecular process may induce a configurational, $\Delta\Delta \rightleftarrows \Lambda\Lambda$, exchange process that, however, can only be observed in the ^{1}H NMR spectrum of the silver(I) complex with the (*R*,*S*)-cyclohexanediyl bridges where 6-R is H. The rates of these exchanges strongly depend on (i) the metal 1B center, M = Ag(I) or Cu(I), (ii) the 6-R substituent in the N_4 ligand, and (iii) the bridging 1,2-alkanediyl groups present. Mechanisms for these intra- and intermolecular exchange processes are proposed.

Introduction

In a previous paper[1] we reported on the solution and solid-state structures of dimeric copper(I) and corresponding silver(I) complexes with the N_4-donor ligands (*R*,*S*)-1,2-(6-R-py-2-CH=N)$_2$Cy (Cy = cyclohexane) (R = H, **1a**; R = Me, **1b**). The molecular geometry of the dication of a representative complex, $[Ag_2(\mu$-(*R*,*S*)-1,2-(py-2-CH=N)$_2$Cy)$_2](O_3SCF_3)_2$ (**2a**), is shown in Figure 1. ^{1}H and ^{13}C NMR studies revealed that these copper(I) and silver(I)

[†] University of Amsterdam.
[‡] Bruker Spectrospin.

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