tween 200 and 500 °C, OH_B groups are mostly eliminated, giving Si–O–Si bridges between layers, which prevent interlayer rehydration and sorption of organic molecules.[6] In sample C, in which the amount of OH groups is lower than in sample D, the capability of rehydration is higher. However, the same thermal treatment of samples A and B does not preclude the subsequent interlayer rehydration and carbonation (basal spacing 14.2 Å), as deduced from infrared and X-ray data. Therefore, it is clear that the interlayer sodium hinders the formation of Si–O–Si bridges between silanol groups of adjacent layers, during the thermal treatment of the samples.

Conclusions

Magadiite is a sodium hydrated hydrogen silicate of lamellar structure that has an excess of sodium hydroxide adsorbed to it. The layers are built up by condensation of two silica tetrahedral sheets,[4,5] and the negative charge of the SiO_4 tetrahedra pointing out of the layer is compensated by sodium ions or by protons, which give silanol groups. The relative proportion of these $Si–O^-Na^+$ and Si–OH groups is approximately 2/3.

The acid treatment of magadiite produces first the neutralization of adsorbed sodium hydroxide and then the exchange of sodium by protons, yielding new Si–OH groups. This treatment increases the interlayer surface density of silanol groups, and the average H–H distances between these groups decrease from ~4 Å in magadiite to ~2.5 Å in H-magadiite. When the silicic acid H-magadiite is obtained, the structure collapses, producing a clear differentiation of the OH groups in two types: those involved in hydrogen bonding between adjacent layers and those that do not interact with the tetrahedral sheet of contiguous layers.

Finally, it is worthwhile to note that silanol groups with both characteristics, short H–H distances and participation in relatively strong hydrogen bonds, have never been observed in amorphous silica and are the consequence of an ordered arrangement of the adjacent layers in the silicic acid H-magadiite.

Acknowledgment. This work was partially supported by a grant from the CAICYT of Spain. We thank Prof. J. M. Serratosa for helpful discussions.

Registry No. Na, 7440-23-5; HCl, 7647-01-0; magadiite, 12285-88-0.

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New Soluble Monomeric Polyselenide Anions, $[MQ(Se_4)_2]^{2-}$ (M = Mo, W; Q = O, S, Se)

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Received December 23, 1987

Reaction of MO_4^{2-} (M = Mo, W) with $[(CH_3)_2(CH_3(CH_2)_7)Si]_2Se$ provides a new synthetic route to the tetraselenometalates MSe_4^{2-}. Reaction of MSe_4^{2-} with Se_8, SeS_2, or $Se_4(NC_5H_{10})_2$ affords the $MQ(Se_4)_2^{2-}$ ion with Q = Se, S, or O, respectively. ^{77}Se NMR studies of this system confirm the general assignment trends of terminal Se (>1200 ppm), "metal bound" Se (1200–600 ppm), and ring Se (<600 ppm). The M = Mo series resonates at lower field than does the M = W series. These trends are in agreement with those seen in ^{17}O and previous ^{77}Se NMR studies. The compound $[NEt_4]_2[MoO(Se_4)_2]$ crystallizes in the monoclinic space group $P2_1/c$ with a = 9.287 (2) Å, b = 17.132 (4) Å, c = 18.353 (4) Å, β = 97.38 (1)°, and Z = 4. The $MoO(Se_4)_2^{2-}$ ion shows square-pyramidal coordination of the Mo^{IV} center by the apical O atom and the two bidentate Se_4^{2-} units. $[PPh_4]_2[WS(Se_4)_2]$ crystallizes in the monoclinic space group $P2_1/a$ with a = 18.366 (7) Å, b = 12.873 (6) Å, c = 20.666 (8) Å, β = 100.74 (1)°, and Z = 4. $WS(Se_4)_2^{2-}$ is structurally analogous to $MoO(Se_4)_2^{2-}$. All of the MSe_4 (M = Mo, W) rings exhibit conformations similar to that of cyclopentane.

Introduction

The relatively rare soluble transition-metal selenide anions ($M_xSe_y^{z-}$) that are currently known in some instances have no direct counterparts among the more common sulfide anions. Those that are analogous to known sulfides include $MoSe_4^{2-}$[1] (vs MoS_4^{2-}[2]), WSe_4^{2-}[3] (vs WS_4^{2-}[2]), $Fe_2Se_{12}^{2-}$[4] (vs $Fe_2S_{12}^{2-}$[4]), $W_3Se_9^{2-}$ and $W_3OSe_8^{2-}$[5] (vs $W_3S_9^{2-}$ and $W_3OS_8^{2-}$[6]), and the unsymmetrical isomer of $W_2Se_{10}^{2-}$[5,7] ($(Se_2)(Se)W(\mu\text{-}Se)_2W(Se)(Se_4)^{2-}$) (vs $W_2S_{10}^{2-}$[8]). Those with no known sulfide analogues include $W_2Se_9^{2-}$,[5,7] symmetrical $W_2Se_{10}^{2-}$ ($(Se_3)(Se)W(\mu\text{-}Se)_2W(Se)(Se_3)^{2-}$),[5,7] and $V_2Se_{13}^{2-}$.[9] Routes to the Mo and W selenides begin with the $MoSe_4^{2-}$[1] or WSe_4^{2-}[3] species, and these in turn were originally prepared from reactions of MoO_3 or WO_3 in concentrated aqueous ammonia solution with excess H_2Se. As the use of excess H_2Se is both expensive and dangerous, we have developed an alternative synthesis of these MSe_4^{2-} (M = Mo, W) ions. This involves the use of bis(dimethyloctylsilyl) selenide ($(dmos)_2Se$) as the source of selenium in place of H_2Se. We describe this alternative synthesis here.

The ions $MQ(S_4)_2^{n-}$ [Q = O, S; M = Mo (n = 2),[10] Re (n = 1)[11]] are known. Here we describe the synthesis and characterization of the ions $MoQ(Se_4)_2^{2-}$ and $WQ(Se_4)_2^{2-}$ (Q = O, S, Se), starting from the MSe_4^{2-} ions. While these Mo selenides are directly analogous to their sulfur counterparts, the W selenides have no known corresponding sulfide analogues.

Experimental Section

All solvents and reagents were used as obtained. Reactions were routinely carried out with the use of standard Schlenk-line procedures under an atmosphere of dry dinitrogen. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, TN, or by Analytical Laboratories, Engelskirchen, FRG. $Na_2MoO_4·2H_2O$, $[NH_4]_2[WO_4]$, and $(CH_3)_2(CH_3(CH_2)_7)SiCl$ were purchased from Aldrich Chemical Co., Milwaukee, WI. Li_2Se was prepared by the method of Gladysz et al.,[12] and $Se_4(NC_5H_{10})_2$ and red selenium (Se_8) were prepared by the method of Foss and Janickis.[13]

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$[(CH_3)_2(CH_3(CH_2)_7)Si]_2Se$. $(CH_3)_2(CH_3(CH_2)_7)SiCl$ (42.6 g, 0.21 mol) was added rapidly to a stirred suspension of Li_2Se (9.5 g, 0.10 mol) in THF (400 mL). After the solution was stirred for 2 days, the THF was removed under vacuum to give a yellow oil and white precipitate. The white LiCl precipitate was removed by filtration, leaving $[(CH_3)_2(CH_3(CH_2)_7)Si]_2Se$ ($(dmos)_2Se$; 38.5 g, 89%) as a clear yellow oil. Anal. Calcd for $C_{20}H_{46}SeSi_2$: C, 57.0; H, 10.9; Se, 18.8; Si, 13.3. Found: C, 57.4; H, 10.8; Se, 18.4; Si, 12.8. ^{77}Se NMR (neat): δ −369. IR (cm^{-1}) (Nujol mull between CsI plates): 1475 (s), 1255 (vs), 845 (vs), 805 (vs), 405 (sh), 375 (s).

$[NH_4]_2[WSe_4]$. A solution of $(dmos)_2Se$ (1.68 g, 4.0 mmol) in toluene (10 mL) was added to a stirred solution of $[NH_4]_2[WO_4]$ (0.28 g, 1.0 mmol) in CH_3CN (15 mL). Over a 2-day period the stirred suspension displayed a series of color changes from pink to red to, finally, brown. The brown solid obtained from the suspension was dissolved in CH_3OH (20 mL) to afford a red solution. This solution was filtered, and to the filtrate was added diethyl ether (20 mL) over a period of 10 min. $[NH_4]_2[WSe_4]$ (0.28 g, 53%) was deposited as golden brown crystals. Anal. Calcd for $H_8N_2Se_4W$: H, 1.5; N, 5.2; Se, 59.0; W, 34.3. Found: H, 1.5; N, 5.3; Se, 58.3; W, 34.6. IR (cm^{-1}): ν(W–Se) 300 (s).

$[NEt_4]_2[MoSe_4]$. A solution of $(dmos)_2Se$ (1.68 g, 4.0 mmol) in toluene (10 mL) was added dropwise over a period of 10 min to a stirred solution of $Na_2MoO_4 \cdot 2H_2O$ (0.24 g, 1.0 mmol) and $[NEt_4]Cl$ (0.33 g, 2.0 mmol) in CH_3CN (15 mL) and NEt_3 (15 mL). The solution displayed a series of color changes from yellow to red-brown to, finally, dark purple. After the solution was stirred for 2 days, $[NEt_4]_2[MoSe_4]$ (0.30 g, 45%) was deposited as purple crystals. Anal. Calcd for $C_{16}H_{40}MoN_2Se_4$: C, 28.6; H, 6.0; Mo, 14.3; N, 4.2; Se, 47.0. Found: C, 27.6; H, 6.2; Mo, 13.6; N, 4.0; Se, 47.3. IR (cm^{-1}): ν(Mo–Se) 338 (s). This material was collected by filtration, washed with two portions of diethyl ether (5 mL), and recrystallized from DMF/diethyl ether. Attempts to grow crystals suitable for X-ray crystallographic analysis by layering diethyl ether over a DMF solution (2 mL) of the crude product (0.15 g) in an 8-mm-diameter tube resulted in a color change of the solution from purple to black-brown in 1 day and the growth of black-purple crystals within 10 days. These crystals were shown to be $[NEt_4]_2[MoO(Se_4)_2]$ by single-crystal X-ray analysis. A second crop from the recrystallization of the crude material contained both $MoSe(Se_4)_2^{2-}$ and $MoO(Se_4)_2^{2-}$ ions when it was examined by ^{77}Se NMR and IR spectroscopy (ν(Mo–O) 928 (s) cm^{-1}).

$[AsPh_4]_2[WSe(Se_4)_2]$. $[NH_4]_2[WSe_4]$ (0.20 g, 0.37 mmol), $[AsPh_4]Cl$ (0.31 g, 0.74 mmol), and red Se_8 (0.18 g, 0.28 mmol) were suspended in DMF (5 mL). CS_2 (5 mL) was added rapidly with stirring. The red Se_8 dissolved immediately, and the solution changed in color from pink to deep red-brown. After it was stirred for 10 min, the solution was filtered to remove any unreacted Se_8, and diethyl ether (40 mL) was added over a period of 10 min. $[AsPh_4]_2[WSe(Se_4)_2]$ (0.50 g, 81%) was deposited as a dark brown crystalline solid. Anal. Calcd for $C_{48}H_{40}As_2Se_9W$: C, 34.7; H, 2.4; As 9.0; Se, 42.8; W, 11.1. Found: C, 33.1; H, 2.5; As, 9.7; Se, 38.4; W, 11.3. IR (cm^{-1}): ν(W–Se) 320 (w). This material was shown to contain small amounts of $WO(Se_4)_2^{2-}$ (~15%) and $WS(Se_4)_2^{2-}$ (~5%) ions when it was analyzed by ^{77}Se NMR and IR spectroscopy (ν(W–O) 933 (w), ν(W–S) 500 (w) cm^{-1}).

$[NEt_4]_2[MoSe(Se_4)_2]$. This Mo analogue was prepared in a similar manner from $[NEt_4]_2[MoSe_4]$ (0.2 g, 0.30 mmol) with the omission of $[AsPh_4]Cl$ from the reaction mixture. $[NEt_4]_2[MoSe(Se_4)_2]$ (0.11 g, 56%) was produced as a dark brown crystalline solid. Anal. Calcd for $C_{16}H_{40}MoN_2Se_9$: C, 18.0; H, 3.7; Mo, 9.0; N, 2.6; Se, 66.6. Found: C, 17.8; H, 3.6; Mo, 9.3; N, 2.6; Se, 66.4. IR (cm^{-1}): ν(Mo–Se) 360 (m).

$[AsPh_4]_2[WS(Se_4)_2]$. DMF (10 mL) was added to $[NH_4]_2[WSe_4]$ (0.20 g, 0.37 mmol), $[AsPh_4]Cl$ (0.16 g, 0.38 mmol), and SeS_2 (0.053 g, 0.37 mmol). This mixture was stirred for 10 min, during which time the orange SeS_2 dissolved and the solution changed in color from pink to deep red-brown. The mixture was filtered to remove any unreacted SeS_2, and diethyl ether (40 mL) was added over a period of 10 min. $[AsPh_4]_2[WS(Se_4)_2]$ (0.26 g, 43%) was deposited as dark purple-brown crystals. Anal. Calcd for $C_{48}H_{40}As_2SSe_8W$: C, 35.7; H, 2.5; As, 9.3; S, 2.0; Se, 39.2; W, 11.4. Found: C, 33.9; H, 2.8; As, 8.7; S, 1.8; Se, 36.8; W, 11.8. IR (ν(W–O) 933 (w), ν(W–S) 504 (m) cm^{-1}) and ^{77}Se NMR spectroscopy indicated the presence of $WO(Se_4)_2^{2-}$ (~15%) in addition to $WS(Se_4)_2^{2-}$.

$[NEt_4]_2[MoS(Se_4)_2]$. This Mo analogue was prepared in a similar manner from $[NEt_4]_2[MoSe_4]$ (0.2 g, 0.30 mmol) with the omission of $[AsPh_4]Cl$ from the reaction mixture. $[NEt_4]_2[MoS(Se_4)_2]$ (0.15 g, 49%) was deposited as brown crystals. Anal. Calcd for $C_{16}H_{40}MoN_2SSe_8$: C, 18.8; H, 3.9; N, 2.7. Found: C, 19.1; H, 4.0; N, 2.8. IR (cm^{-1}): ν(Mo–S) 515 (s).

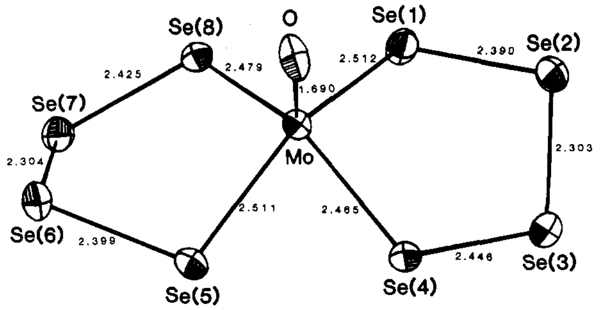

Figure 1. Structure of the $MoO(Se_4)_2^{2-}$ ion. Here and in Figure 2 the 50% probability ellipsoids are shown.

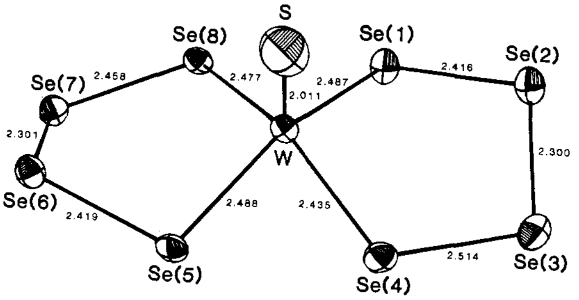

Figure 2. Structure of the $WS(Se_4)_2^{2-}$ ion.

$[AsPh_4]_2[WO(Se_4)_2]$. DMF (10 mL) was added to $[NH_4]_2[WSe_4]$ (0.20 g, 0.37 mmol), $[AsPh_4]Cl$ (0.31 g, 0.74 mmol), and $Se_4(NC_5H_{10})_2$ (0.36 g, 0.74 mmol) with stirring. The solution turned deep red-brown rapidly. After 15 min it was filtered and diethyl ether (40 mL) was added over a period of 10 min. $[AsPh_4]_2[WO(Se_4)_2]$ (0.51 g, 86%) was deposited as dark-brown crystals. Anal. Calcd for $C_{48}H_{40}As_2OSe_8W$: C, 36.0; H, 2.5; As, 9.4; Se, 39.5; W, 11.5. Found: C, 35.9; H, 2.5; As, 9.4; Se, 44.7; W, 11.3. IR (cm^{-1}): ν(W–O) 931 (s).

$[NEt_4]_2[MoO(Se_4)_2]$. This Mo analogue was prepared in a similar manner from $[NEt_4]_2[MoSe_4]$ (0.20 g, 0.30 mmol) with the omission of $[AsPh_4]Cl$ from the reaction mixture. $[NEt_4]_2[MoO(Se_4)_2]$ (0.27 g, 90%) was deposited as dark brown crystals. Anal. Calcd for $C_{16}H_{40}MoN_2OSe_8$: C, 19.1; H, 4.0; Mo, 9.6; N, 2.8; O, 1.6; Se, 62.9. Found: C, 18.8; H, 3.9; Mo, 8.9; N, 2.9; Se, 64.0. IR (cm^{-1}): ν(Mo–O) 928 (s).

Physical Measurements. Unless noted otherwise, the IR spectra were obtained as KBr pellets on a Perkin-Elmer 283 spectrophotometer. The ^{77}Se NMR spectra were recorded with the use of a Varian XLA-400 spectrometer and techniques described in detail elsewhere.[5] Chemical shifts are referenced relative to Me_2Se at 0 ppm.

Crystallographic Studies of $[NEt_4]_2[MoO(Se_4)_2]$ and $[AsPh_4]_2[WS(Se_4)_2]$. A given crystal was mounted on a glass fiber and placed on an Enraf-Nonius CAD4 diffractometer. The unit cell was determined from 25 automatically centered reflections. The crystal was then transferred into the cold stream (−150 °C) of a Picker FACS-1 diffractometer for data collection. No significant change in the intensities of six standard reflections, monitored every 100 reflections during data collection, was observed. Hence, the crystal was stable in the nitrogen cold stream. Crystal data and data collection parameters are given in Table I.

In the solution and refinement of these structures, procedures standard in this laboratory were employed.[14] In the solution of the structure of $[NEt_4]_2[MoO(Se_4)_2]$ the positions of the Mo and the eight Se atoms were determined by direct methods. The remaining non-hydrogen atomic positions were determined from subsequent electron density syntheses. Each of the methylene C atoms for one of the NEt_4^+ groups was found to be disordered over two sites. The occupancies were refined with their sum set to unity and linked to the occupancies of C atoms in the other methylene groups in this NEt_4^+ ion. This resulted in occupancies of 0.56 (1) and 0.44 (1) for C atoms in these sites. The methyl C atoms showed no signs of disorder. Standard Patterson and electron density techniques were used in the solution of the structure of $[AsPh_4]_2[WS(Se_4)_2]$. Both structures were refined by full-matrix least-squares methods. The final cycles of refinement were carried out on F_o^2. Prior to these final cycles, H atoms were included at calculated positions (C–H = 0.95 Å). The methyl hydrogen atoms in $[NEt_4]_2[MoO(Se_4)_2]$ were located in a difference electron density map, and their positions were idealized. Each

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[13] (a) Foss, O.; Janickis, V. *J. Chem. Soc., Chem. Commun.* **1977**, 833–834. (b) *Ibid* **1977**, 834–835.

[14] See, for example: Waters, J. M.; Ibers, J. A. *Inorg. Chem.* **1977**, *16*, 3273–3277.

Table I. Crystal Data and Experimental Details[a]

compd	$[NEt_4]_2[MoO(Se_4)_2]$	$[AsPh_4]_2[WS(Se_4)_2]$
formula	$C_{16}H_{40}MoN_2OSe_8$	$C_{48}H_{40}As_2Se_8SW$
fw	1004	1614
a, Å	9.287 (2)	18.366 (7)
b, Å	17.132 (4)	12.873 (6)
c, Å	18.353 (4)	20.666 (8)
β, deg	97.38 (1)	100.74 (1)
V, Å^3	2896	4800
Z	4	4
temp, °C[b]	−150	−150
d_{calcd}, g/cm^3 (−150 °C)	2.303	2.233
space group	C_{2h}^5-$P2_1/c$	C_{2h}^5-$P2_1/a$
cryst shape	parallelepiped bounded by {100}, {011}	plate bounded by {001}, (010), (100), $(0\bar{2}\bar{1})$, (201), $(\bar{2}01)$
cryst dimens, mm	0.42 × 0.28 × 0.26	0.40 × 0.27 × 0.12
cryst, vol, mm^3	0.0304	0.0094
μ, cm^{-1}	104.1	99.04
transmission factors[c]	0.073–0.140	0.145–0.352
takeoff angle, deg	2.0	2.0
receiving aperture, mm	4.5 × 4.5	4.0 × 4.0
scan type	θ	θ
scan speed, deg/min	1.0	1.0
scan range, deg	1.8	1.8
data collected	$+h,+k,\pm l$; $3.0 \leq 2\theta \leq 53.0°$	$+h,+k,\pm l$; $3.0 \leq 2\theta \leq 46.0°$
ρ factor	0.04	0.04
no. of unique data	6650	8786
no. of unique data with $F_o^2 > 3\sigma(F_o^2)$	3892	5513
no. of variables	285	301
R on F_o^2	0.090	0.080
R_w on F_o^2	0.111	0.109
R on $F_o(F_o^2 > 3\sigma(F_o^2))$	0.072	0.047
R_w on $F_o(F_o^2 > 3\sigma(F_o^2))$	0.078	0.048
error in observn of unit wt, e^2	1.30	1.07

[a] All data were collected with Mo Kα radiation on a Picker FACS-1 diffractometer operated under the Vanderbilt disk-oriented system: Lenhert, P. G. *J. Appl. Crystallogr.* **1975**, *8*, 568–570. Peaks with $\sigma(I)/I > 0.333$ were rescanned. [b] The low-temperature system is based on a design by: Huffman, J. C. Ph.D. Thesis, Indiana University, 1974. [c] An analytical absorption correction was applied: de Meulenaer, J.; Tompa, H. *Acta Crystallogr.* **1965**, *19*, 1014–1018.

Table II. Positional Parameters and Equivalent Isotropic Thermal Parameters for $[NEt_4]_2[MoO(Se_4)_2]$

atom	x	y	z	B_{eq}, Å^2
Mo(1)	0.653 974 (87)	0.117 511 (49)	0.785 075 (44)	1.38 (2)
Se(1)	0.648 31 (11)	−0.011 240 (59)	0.719 371 (53)	1.79 (2)
Se(2)	0.565 18 (11)	0.019 341 (65)	0.593 895 (54)	2.16 (3)
Se(3)	0.742 60 (11)	0.107 000 (65)	0.571 925 (54)	2.14 (3)
Se(4)	0.743 11 (11)	0.187 312 (59)	0.682 211 (53)	1.78 (3)
Se(5)	0.810 06 (12)	0.221 556 (62)	0.851 250 (56)	2.20 (3)
Se(6)	0.791 42 (11)	0.202 060 (60)	0.979 242 (55)	1.88 (3)
Se(7)	0.877 66 (11)	0.075 966 (63)	0.988 342 (53)	1.97 (3)
Se(8)	0.725 62 (11)	0.020 902 (58)	0.883 603 (52)	1.70 (2)
O(1)	0.479 11 (67)	0.143 02 (39)	0.788 37 (33)	1.9 (2)
N(1)	0.302 15 (81)	0.246 60 (47)	−0.009 28 (46)	1.9 (2)
N(2)	−0.158 02 (83)	0.038 79 (46)	0.250 85 (42)	1.7 (2)
C(1)	0.384 0 (11)	0.280 43 (57)	−0.069 00 (55)	2.0 (3)
C(2)	0.296 1 (13)	0.281 57 (70)	−0.143 60 (60)	3.4 (3)
C(3)	0.160 7 (11)	0.288 28 (71)	−0.005 35 (59)	3.0 (3)
C(4)	0.174 6 (12)	0.375 46 (73)	0.009 28 (68)	3.7 (4)
C(5)	0.403 1 (10)	0.256 82 (57)	0.061 69 (54)	1.9 (3)
C(6)	0.343 3 (12)	0.229 14 (64)	0.131 16 (54)	2.4 (3)
C(7)	0.265 0 (11)	0.161 90 (63)	−0.023 54 (55)	2.4 (3)
C(8)	0.389 4 (13)	0.109 00 (60)	−0.035 52 (57)	2.7 (3)
C(9A)	−0.226 9 (17)	−0.039 95 (91)	0.249 24 (89)	1.3 (4)
C(98)	−0.047 9 (24)	−0.030 6 (13)	0.253 9 (13)	2.2 (6)
C(10)	−0.119 6 (11)	−0.106 58 (68)	0.270 12 (60)	2.9 (3)
C(11A)	−0.051 5 (17)	0.045 6 (10)	0.197 80 (94)	1.7 (4)
C(11B)	−0.072 1 (21)	0.109 8 (12)	0.248 9 (11)	1.5 (4)
C(12)	0.006 1 (10)	0.124 25 (63)	0.185 17 (52)	2.2 (3)
C(13A)	−0.085 4 (19)	0.060 4 (10)	0.326 15 (89)	1.9 (5)
C(13B)	−0.237 3 (23)	0.035 3 (14)	0.312 4 (12)	2.0 (6)
C(14)	−0.164 2 (15)	0.051 54 (75)	0.386 67 (60)	4.2 (4)
C(15A)	−0.283 4 (18)	0.099 2 (10)	0.232 40 (87)	1.7 (4)
C(15B)	−0.254 4 (28)	0.022 6 (16)	0.179 1 (13)	3.1 (7)
C(16)	−0.361 3 (12)	0.091 57 (65)	0.159 16 (60)	2.7 (3)

hydrogen atom was given a thermal parameter (B_{iso}) 1 Å^2 greater than the carbon atom to which it is attached. The results of the refinements are given in Table I. The final positional parameters and equivalent isotropic thermal parameters of all non-hydrogen atoms are given in Tables II and III. Additional crystallographic data are available as supplementary material.[15] The $MoO(Se_4)_2^{2-}$ and $WS(Se_4)_2^{2-}$ ions are illustrated in Figures 1 and 2.

Results

Synthesis. Müller and co-workers first prepared $MoSe_4^{2-}$ as its ammonium salt by passing H_2Se into an aqueous ammonia solution of MoO_3.[1] WSe_4^{2-} has been prepared from WO_3 in a similar manner by Lenher and Fruehan.[3] We investigated the use of $(Me_3Si)_2Se$, $(dmos)_2Se$ (dmos = dimethyloctylsilyl), and $(Ph_3Si)_2Se$ as possible "selenation" agents to replace H_2Se. $(Me_3Si)_2Se$ is volatile and, thus, was difficult to handle, and $(Ph_3Si)_2Se$, being a solid, was difficult to separate from the resulting products and displayed poor reactivity. $(dmos)_2Se$ represents a compromise, as it is nonvolatile liquid. For this reason it was selected for a detailed investigation. Its synthesis was readily accomplished by stirring Li_2Se with (dmos)Cl for 2 days. If Li_2Se prepared by reaction of Li and Se in liquid ammonia is used, only 1 day of stirring is needed. We find that the tetraselenometalates MSe_4^{2-} (M = Mo, W) can be synthesized readily as their NH_4^+ or NEt_4^+ salts by the reaction of $(dmos)_2Se$ with the corresponding oxometalates, MO_4^{2-}. For M = Mo and a MoO_4^{2-}:$(dmos)_2Se$ ratio of 1:4, a mixture of products is formed. NMR spectroscopy on a solution of the crude material suggested the presence of $MoSe_4^{2-}$, $MoO(Se_4)_2^{2-}$, and $MoSe(Se_4)_2^{2-}$. Rapid recrystallization leads to pure $[NEt_4]_2[MoSe_4]$, with $[NEt_4]_2[MoO(Se_4)_2]$ and $[NEt_4]_2[MoSe(Se_4)_2]$ being concentrated in the supernatant solution. Slow recrystallization in narrow tubes over a period of several weeks leads to $[NEt_4]_2[MoO(Se_4)_2]$, whose structure was determined by X-ray crystallographic analysis. No attempts were made to purify any of the solvents used, since there are other possible sources of water in the reactions, e.g., $Na_2MoO_4 \cdot 2H_2O$ and $[AsPh_4]Cl \cdot xH_2O$.[16]

In addition to the syntheses of these monomeric chalcogenides, we have used $(dmos)_2Se$ successfully in the synthesis of the $V_2Se_{13}^{2-}$ ion. Similarly, Holm and co-workers[17,18] have employed $(Me_3Si)_2S$ in the synthesis of a number of sulfide-containing anions. Interestingly, reaction of MoO_4^{2-} with $(Me_3Si)_2S$ does not give MoS_4^{2-} but rather a series of stepwise substitution products whose terminal member is $MoS_3(OSiMe_3)^-$.[19]

In order to extend the chemistry of tungsten selenides and to provide a rational synthesis of $[NEt_4]_2[MoO(Se_4)_2]$, the reactions of the MSe_4^{2-} (M = Mo, W) anions with selenium-containing reagents have been investigated. The WSe_4^{2-} anion reacts with $^3/_4$ equiv of red Se_8 in the presence of 2 equiv of $[AsPh_4]Cl$ to afford the $WSe(Se_4)_2^{2-}$ species. Addition of CS_2 to the reaction mixture promotes the solubility of Se_8 but causes the incorporation of sulfur into the product. ^{77}Se NMR and IR spectroscopies were used to show the presence of small amounts of $WS(Se_4)_2^{2-}$ and $WO(Se_4)_2^{2-}$ ions in the product.

^{77}Se NMR and IR spectroscopies were used to follow the reaction of WSe_4^{2-} with SeS_2 in the presence of 1 equiv of $[AsPh_4]Cl$ in DMF solvent. $WS(Se_4)_2^{2-}$ is the major product, but $WO(Se_4)_2^{2-}$ is also produced as a minor component. The optimum

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(15) For supplementary material available, see paragraph at the end of this paper.

(16) The preparation of $MoSe_4^{2-}$ and WSe_4^{2-} by reaction of the corresponding $M(CO)_6$ species with a polyselenide solution has recently been described (O'Neal, S. C.; Kolis, J. W. *J. Am. Chem. Soc.* **1988**, *110*, 1971–1973).

(17) Sola, J.; Do, Y.; Berg, J. M.; Holm, R. H. *Inorg. Chem.* **1985**, *24*, 1706–1713.

(18) Do, Y.; Simhon, E. D.; Holm, R. H. *Inorg. Chem.* **1985**, *24*, 1831–1838.

(19) O'Neal and Kolis have recently prepared $MoSe(Se_4)_2^{2-}$ by the same route. See ref 16.

Table III. Positional Parameters and Equivalent Isotropic Thermal Parameters for $[AsPh_4]_2[WS(Se_4)_2]$

atom	*x*	*y*	*z*	B_{eq}, Å^2
W(1)	0.107 948 (21)	0.068 519 (34)	0.229 614 (21)	1.44 (1)
Se(1)	0.202 899 (55)	0.044 412 (90)	0.331 267 (54)	2.03 (3)
Se(2)	0.150 950 (58)	0.110 008 (91)	0.422 389 (56)	2.15 (3)
Se(3)	0.038 383 (61)	0.026 445 (93)	0.408 075 (58)	2.38 (3)
Se(4)	0.007 330 (54)	0.016 667 (89)	0.284 507 (56)	2.05 (3)
Se(5)	0.022 933 (53)	−0.018 547 (90)	0.137 821 (54)	1.93 (3)
Se(6)	0.080 814 (55)	0.004 251 (88)	0.042 796 (53)	1.89 (3)
Se(7)	0.194 459 (53)	−0.071 112 (90)	0.080 326 (53)	1.87 (3)
Se(8)	0.219 696 (51)	0.002 121 (84)	0.192 093 (52)	1.67 (3)
S(1)	0.095 95 (20)	0.221 20 (30)	0.209 82 (19)	4.3 (1)
As(1)	−0.375 106 (51)	0.065 700 (85)	0.436 568 (51)	1.43 (3)
As(2)	0.305 675 (56)	0.090 942 (83)	−0.099 683 (55)	1.73 (3)
C(1)	−0.368 76 (49)	−0.076 95 (77)	0.462 97 (47)	1.4 (2)
C(2)	−0.364 90 (52)	−0.105 37 (78)	0.528 10 (50)	1.7 (2)
C(3)	−0.365 39 (57)	−0.210 48 (86)	0.542 68 (54)	2.2 (2)
C(4)	−0.369 77 (52)	−0.283 47 (79)	0.495 34 (50)	1.9 (2)
C(5)	−0.371 58 (54)	−0.255 61 (82)	0.430 10 (52)	1.9 (2)
C(6)	−0.369 68 (54)	−0.150 95 (84)	0.414 55 (53)	2.1 (2)
C(7)	−0.296 60 (52)	0.083 77 (80)	0.387 62 (50)	1.8 (2)
C(8)	−0.233 53 (53)	0.022 46 (80)	0.405 66 (50)	1.8 (2)
C(9)	−0.176 47 (55)	0.031 32 (82)	0.369 35 (53)	2.1 (2)
C(10)	−0.184 14 (58)	0.094 34 (87)	0.316 44 (56)	2.4 (2)
C(11)	−0.247 28 (59)	0.153 03 (90)	0.298 50 (57)	2.6 (2)
C(12)	−0.303 47 (57)	0.151 95 (88)	0.335 06 (55)	2.2 (2)
C(13)	−0.470 12 (47)	0.088 37 (71)	0.379 11 (46)	1.2 (2)
C(14)	−0.520 61 (52)	0.006 90 (80)	0.369 13 (50)	1.8 (2)
C(15)	−0.586 26 (53)	0.020 32 (82)	0.324 01 (51)	1.8 (2)
C(16)	−0.599 22 (53)	0.112 58 (82)	0.290 52 (51)	1.8 (2)
C(17)	−0.549 19 (54)	0.194 74 (82)	0.300 86 (52)	1.8 (2)
C(18)	−0.483 86 (52)	0.182 07 (80)	0.347 68 (50)	1.7 (2)
C(19)	−0.369 69 (51)	0.151 06 (78)	0.513 77 (49)	1.5 (2)
C(20)	−0.305 57 (52)	0.147 42 (82)	0.561 96 (51)	1.8 (2)
C(21)	−0.302 77 (57)	0.202 83 (87)	0.620 06 (55)	2.3 (2)
C(22)	−0.363 07 (53)	0.262 02 (81)	0.628 29 (51)	2.0 (2)
C(23)	−0.425 09 (53)	0.265 40 (80)	0.580 40 (51)	1.8 (2)
C(24)	−0.429 52 (54)	0.211 06 (82)	0.522 84 (52)	1.8 (2)
C(25)	0.369 94 (50)	0.111 08 (77)	−0.016 28 (48)	1.4 (2)
C(26)	0.369 64 (61)	0.042 68 (91)	0.034 53 (58)	2.6 (2)
C(27)	0.417 37 (63)	0.060 0 (10)	0.094 69 (61)	3.0 (2)
C(28)	0.462 80 (64)	0.145 6 (10)	0.102 08 (62)	3.1 (2)
C(29)	0.464 18 (60)	0.215 37 (89)	0.050 97 (57)	2.5 (2)
C(30)	0.418 93 (56)	0.196 04 (85)	−0.008 23 (54)	2.2 (2)
C(31)	0.268 53 (57)	−0.048 80 (87)	−0.106 63 (54)	2.0 (2)
C(32)	0.193 61 (54)	−0.063 23 (87)	−0.127 34 (52)	2.0 (2)
C(33)	0.165 86 (59)	−0.163 68 (90)	−0.136 25 (57)	2.6 (2)
C(34)	0.213 46 (61)	−0.247 31 (93)	−0.124 29 (57)	2.6 (2)
C(35)	0.287 78 (60)	−0.230 21 (90)	−0.103 81 (57)	2.5 (2)
C(36)	0.317 43 (56)	−0.131 71 (86)	−0.093 67 (54)	2.1 (2)
C(37)	0.220 04 (49)	0.177 01 (75)	−0.107 72 (47)	1.4 (2)
C(38)	0.183 52 (55)	0.180 32 (83)	−0.055 20 (53)	2.1 (2)
C(39)	0.117 27 (59)	0.235 53 (88)	−0.060 52 (56)	2.4 (2)
C(40)	0.091 23 (56)	0.285 53 (85)	−0.118 55 (54)	2.3 (2)
C(41)	0.129 30 (63)	0.288 86 (96)	−0.170 16 (60)	2.9 (2)
C(42)	0.194 37 (58)	0.231 03 (87)	−0.165 00 (56)	2.3 (2)
C(43)	0.361 30 (52)	0.116 19 (79)	−0.168 27 (51)	1.6 (2)
C(44)	0.375 49 (57)	0.216 93 (87)	−0.185 43 (55)	2.2 (2)
C(45)	0.421 79 (55)	0.234 42 (83)	−0.232 16 (52)	1.9 (2)
C(46)	0.454 10 (51)	0.149 10 (80)	−0.256 49 (50)	1.6 (2)
C(47)	0.439 39 (54)	0.050 58 (83)	−0.239 03 (52)	1.8 (2)
C(48)	0.391 26 (54)	0.031 94 (82)	−0.194 73 (52)	2.0 (2)

WSe_4^{2-}:SeS_2 stoichiometry for the reaction is 1:1, and the yield of $[AsPh_4]_2[WS(Se_4)_2]$ is always less than 50%. Upon addition of a further 1 equiv of $[AsPh_4]Cl$ to the supernatant liquid after the isolation of $[AsPh_4]_2[WS(Se_4)_2]$, an orange solid was obtained. This material exhibits IR bands at 446 (ν(W–S)) and 295 cm^{-1} (ν(W–Se)) and ^{77}Se NMR lines at δ 1100 and 1024 (terminal Se atoms). Elemental analytical results demonstrated the presence of both sulfur and selenium. These data suggest that this material is a monomeric selenosulfidotungstate. Possible reaction pathways, therefore, are

$$2WSe_4^{2-} + 2SeS_2 \rightarrow WS(Se_4)_2^{2-} + WS_2Se_2^{2-} + {}^1/_8S_8$$

$$2WSe_4^{2-} + 2SeS_2 \rightarrow WS(Se_4)_2^{2-} + WS_3Se^{2-} + {}^1/_8Se_8$$

Table IV. Selected Bond Distances (Å) and Bond Angles (deg) in the $MoO(Se_4)_2^{2-}$ and $WS(Se_4)_2^{2-}$ Ions

	$MoO(Se_4)_2^{2-}$	$WS(Se_4)_2^{2-}$
M–Se(1)	2.512 (1)	2.487 (1)
M–Se(4)	2.465 (1)	2.435 (1)
M–Se(5)	2.511 (1)	2.488 (1)
M–Se(8)	2.479 (1)	2.477 (1)
M–Q	1.690 (6)	2.011 (4)
Se(1)–Se(2)	2.390 (1)	2.416 (2)
Se(2)–Se(3)	2.303 (2)	2.300 (2)
Se(3)–Se(4)	2.446 (2)	2.514 (2)
Se(5)–Se(6)	2.399 (2)	2.419 (2)
Se(6)–Se(7)	2.304 (2)	2.301 (2)
Se(7)–Se(8)	2.425 (1)	2.458 (2)
Se(1)–M–Se(4)	92.73 (4)	92.63 (5)
Se(4)–M–Se(5)	78.20 (4)	78.98 (5)
Se(5)–M–Se(8)	92.17 (4)	92.56 (4)
Se(8)–M–Se(1)	75.51 (4)	74.33 (4)
Se(1)–M–Se(5)	146.24 (5)	146.05 (5)
Se(4)–M–Se(8)	142.88 (5)	142.77 (5)
Se(1)–M–Q	106.5 (2)	109.1 (1)
Se(4)–M–O	108.7 (2)	107.4 (1)
Se(5)–M–Q	107.2 (2)	104.8 (1)
Se(8)–M–Q	108.4 (2)	109.8 (1)
M–Se(1)–Se(2)	104.69 (5)	107.35 (5)
Se(1)–Se(2)–Se(3)	99.31 (5)	102.26 (6)
Se(2)–Se(3)–Se(4)	98.51 (5)	100.51 (6)
Se(3)–Se(4)–M	113.23 (5)	114.29 (5)
M–Se(5)–Se(6)	105.33 (5)	104.84 (5)
Se(5)–Se(6)–Se(7)	97.68 (5)	100.57 (6)
Se(6)–Se(7)–Se(8)	98.41 (5)	98.94 (5)
Se(7)–Se(8)–M	113.09 (5)	113.85 (5)

In DMF, $WS(Se_4)_2^{2-}$ is slowly converted to $WO(Se_4)_2^{2-}$ over a period of about 1 week. This interconversion may be followed by ^{77}Se NMR spectroscopy by taking spectra at intervals of 1 day. The reaction of WSe_4^{2-} with 2 equiv of $Se_4(NC_5H_{10})_2$ gives $WO(Se_4)_2^{2-}$ in high yield. The oxygen atom presumably originates from the "wet" DMF solvent.

The reactions of $[NEt_4]_2[MoSe_4]$ with Se_8,[19] SeS_2, and $Se_4(NC_5H_{10})_2$ follow the same course as their W counterparts, and ^{77}Se NMR spectroscopy showed that the products contain less of the minor components in the mixtures. By comparison, Draganjac et al. have shown that $MoS(S_4)_2^{2-}$ may be synthesized from MoS_4^{2-} and sulfur or "active" sulfur reagents, such as organic trisulfides, in dry DMF or acetonitrile. Upon hydrolysis, $MoS(S_4)_2^{2-}$ is converted to $MoO(S_4)_2^{2-}$.[10] This suggests that the ligand occupying the apical coordination site in this type of structure is labile.

While the $MQ(Se_4)_2^{2-}$ ions (M = Mo, W) are analogous to known sulfide ions,[10,11] the W compounds have no known sulfur analogues. Indeed, reaction of WS_4^{2-} with S_8 affords only $W_2S_{12}^{2-}$,[20] while MoS_4^{2-} reacts with S_8 to afford either $Mo_2S_{12}^{2-}$[20] or $MoQ(S_4)_2^{2-}$[10] (Q = O, S).

Structures. The two compounds $[NEt_4]_2[MoO(Se_4)_2]$ (Figure 1) and $[AsPh_4]_2[WS(Se_4)_2]$ (Figure 2) (Table IV) contain isostructural anions that are similar to $MoO(S_4)_2^{2-}$,[10] $MoS(S_4)_2^{2-}$,[10] $MoSe(Se_4)_2^{2-}$,[19] $ReO(S_4)_2^{-}$,[11] and $ReS(S_4)_2^{-}$.[11] All these ions show square-pyramidal coordination about the central metal atom. In the present $MoOSe_4$ and $WSSe_4$ square pyramids, the metal atoms are displaced from the basal planes toward the apical O or S atoms by 0.760 and 0.754 Å, respectively. Similar displacements by 0.725 and 0.760 Å of the Mo atoms are observed in the compounds $[NEt_4]_2[MoS(S_4)_2]$ and $[NEt_4]_2[MoO(S_4)_2]$.[10]

The Mo–O distance (1.690 (6) Å) in $[NEt_4]_2[MoO(Se_4)_2]$ is very similar to that distance in $[NEt_4]_2[MoO(S_4)_2]$ (1.685 (7) Å).[10] The W–S distance (2.011 (4) Å) in $[AsPh_4]_2[WS(Se_4)_2]$ is close to that in $[PPh_4]_2[W_3S_9]$ (2.070 (10) Å) involving the central W atom and the apical S atom.[6] The thermal parameters, however, for the S atom (B_{eq} = 4.3 (1) Å^2) in $[AsPh_4]_2[WS(Se_4)_2]$ are somewhat higher than was expected. This possibly indicates the occurrence of O/S disorder at this site similar to that present

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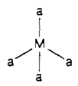
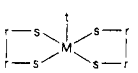
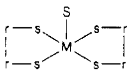
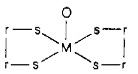
(20) Cohen, S. A.; Stiefel, E. I. *Inorg. Chem.* **1985**, *24*, 4657–4662.

Table V. ^{77}Se NMR Spectroscopic Data Measured in DMF Solvent, Ph_2Se_2/C_6D_6 External Standard: δ ($^1J_{Se-W}$ = Hz)

			M = Mo	M = W
MSe_4^{2-}		a	1643	1235 (52)
$MSe(Se_4)_2^{2-}$		t	2357	1787[a]
		s	1163	1034 (108)
		r	403	324
$MS(Se_4)_2^{2-}$		s	1122	993 (106)
		r	396	313
$MO(Se_4)_2^{2-}$		s	946	828 (98)
		r	380	280

[a] No W satellites were observed for terminal Se nuclei.

in the rhenium sulfide, $[PPh_4][ReS(S_4)_2]_{0.7}[ReO(S_4)_2]_{0.3}$.[11] No attempts were made to model this disorder, and no unusual thermal parameters were found for the apical O atom in $[NEt_4]_2[MoO(Se_4)_2]$.

In $[NEt_4]_2[MoO(Se_4)_2]$ and $[AsPh_4]_2[WS(Se_4)_2]$ the individual Mo–Se and W–Se distances (average values of 2.49 (2) and 2.47 (3) Å, respectively) differ significantly from each other. This effect has also been reported for $MoS(S_4)_2^{2-}$.[10] The tetraselenide ligands show an alternation in the lengths of the Se–Se bonds. The Se(terminal)–Se(internal) bonds (2.41 (3) Å for $MoO(Se_4)_2^{2-}$ and 2.45 (5) Å for $WS(Se_4)_2^{2-}$) are significantly longer than the Se(internal)–Se(internal) bonds (2.304 (1) and 2.301 (1) Å), as in $MoSe(Se_4)_2^{2-}$[19] and $W_2Se_{10}^{2-}$.[7,5] Block and Allmann have proposed that M(dπ)–S(dπ) interactions cause this effect in the $MoS_4(C_5H_5)_2$ complex.[21] The MSe_4 rings have puckered geometries similar to that of their organic counterpart, cyclopentane. The two rings on a particular ion of $MoO(Se_4)_2^{2-}$ and $WS(Se_4)_2^{2-}$ are puckered in opposite directions, giving rise to chiral units.

Spectroscopy. The metal–selenide compounds show ν(M–Se) vibrations in the range 360–600 cm^{-1}, and the compounds containing sulfide and oxide ligands exhibit ν(M–S) and ν(M–O) at 520–500 and 940–920 cm^{-1}, respectively (see Experimental Section). The electronic spectra of $[NEt_4]_2[MoSe_4]$ (640, 566, 367 nm) and $[NEt_4]_2[WSe_4]$ (525, 470, 318 nm) do not differ from those reported by Müller and Diemann,[22] while those of the $MQSe_8^{2-}$ anions display no characteristic absorption bands. Similarly, the soluble tungsten–selenide anions $W_3Se_9^{2-}$, $W_2Se_9^{2-}$, and $W_2Se_{10}^{2-}$ [5] show no characteristic bands.

In Table V the chemical shift and coupling constant data are summarized for the molybdenum and tungsten selenides and their sulfido and oxo derivatives. We have reported preliminary results of this investigation for the $WS(Se_4)_2^{2-}$ anion.[5] We have shown that resonances corresponding to Se atoms directly bound to W (^{183}W, $I = {}^1/_2$, abundance 14.3%) exhibit W satellites, whereas Se atoms not directly bound to W show much weaker satellites owing to coupling to Se (^{77}Se, $I = {}^1/_2$, abundance 7.6%). Often, the latter Se–Se satellites are not observed. In this way we may distinguish "W-bound Se" atoms and "ring Se" atoms. We have found that the former type of Se atoms resonate in the range of about 1200–600 ppm whereas the latter kind lie in the higher field range of approximately 600–200 ppm. The $MQ(Se_4)_2^{2-}$ series of compounds fall into this regime. Since only one resonance is observed for each type of site for each compound, the puckered five-membered rings are fluxional at room temperature in solution. No change in ^{77}Se NMR peak shapes or positions was seen on cooling the $MoQ(Se_4)_2^{2-}$ anions to −60 °C in DMF solution. In Figure 3a the ^{77}Se NMR spectrum in the "W-bound Se" range is shown for the $WQ(Se_4)_2^{2-}$ (Q = Se, S, O) system obtained from the reaction of WSe_4^{2-} with $^3/_4$ equiv of red Se_8 in DMF/CS_2. The reaction mixture containing mainly $WQ(Se_4)_2^{2-}$ (Q = S, O) from the reaction of WSe_4^{2-} with SeS_2 in DMF yields a spectrum in which the line at 1034 ppm is much diminished in intensity (Figure 3b). The compound $WO(Se_4)_2^{2-}$ from the reaction of WSe_4^{2-} with $Se_4(NC_5H_{10})_2$ has only a single line at 828 ppm (Figure 3c) in this range. The lines in the "ring Se" region for these systems show similar intensity patterns. In this way the assignments in Table V were made. The resonances at 1787 and 2357 ppm may be assigned to the apical Se atom in $WSe(Se_4)_2^{2-}$ and $MoSe(Se_4)_2^{2-}$, respectively, since they occur at the low-field end of the range. This low-field shift may result from a higher bond order for these MSe apical bonds.

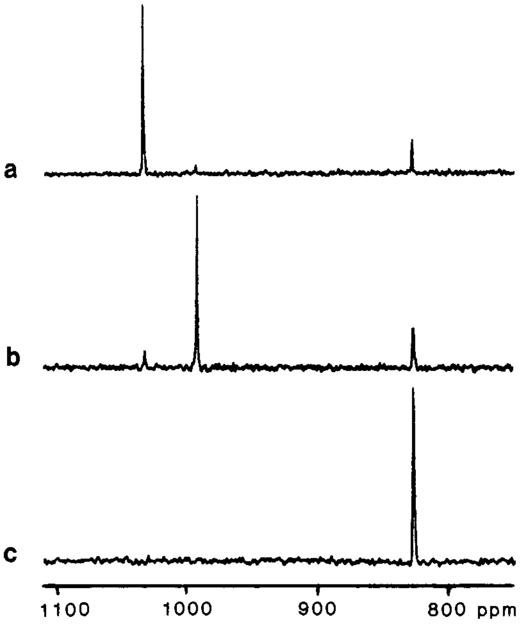


Figure 3. ^{77}Se NMR spectra of the "W-bound Se" region of $WQ(Se_4)_2^{2-}$ (Q = O, S, Se) for three reactions: (a) WSe_4^{2-} + $^3/_4Se_8$ in DMF/CS_2 (major product $WSe(Se_4)_2^{2-}$); (b) WSe_4^{2-} + SeS_2 in DMF (major product $WS(Se_4)_2^{2-}$); (c) WSe_4^{2-} + $Se_4(NC_5H_{10})_2$ in DMF (major product $WO(Se_4)_2^{2-}$).

Comparison of these assignments and the general trends arising from them shows several interesting and consistent parallels with ^{17}O and previous ^{77}Se NMR studies. In the $[Zn_4(SePh)_4(\mu\text{-}SePh)_6]^{2-}$ ion the terminal Se nuclei resonate at lower field (δ = 46.3) than do the bridging Se nuclei (δ = −6.7).[23] ^{17}O NMR studies of early-transition-metal polyoxoanions have revealed definite terminal and bridging regions of the spectrum.[24] Within a given anion, terminal oxygen nuclei resonate at a lower field (higher ppm) than do bridging oxygen nuclei. For example, in $Mo_2O_7^{2-}$ δ[O(terminal)] = 715 and δ[O(bridging)] = 248, and in $Mo_6O_{19}^{2-}$ δ[O(terminal)] = 927 and δ[O(bridging)] = 559.[25] In general, there is a correlation between increasing M–O bond order and decreasing field.[26]

Owing to the similar size of Mo and Se atoms, there may be a greater orbital overlap in the selenomolybdates than in the selenotungstates. This would cause a greater withdrawal of electron density by Mo as compared with W from adjacent selenide ligands. This, in turn, may be the reason for the observed low-field shift of the ^{77}Se resonances of the selenomolybdates relative to those of the selenotungstates. A similar trend is seen in the ^{17}O NMR spectra of the oxoanions MoO_4^{2-} (δ 831) and WO_4^{2-} (δ 420).[27] The orbital overlap may also be greater between Se and S and a metal atom (Mo or W) than between O and Mo or W owing to the availability of low-lying vacant d orbitals on Se and S. This may explain the trend in the chemical shifts of the

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selenides and their sulfide and oxide derivatives.

Acknowledgment. This research was supported by the National Science Foundation (Grant No. CHE-8701007).

Registry No. $[(CH_3)_2(CH_3(CH_2)_7)Si]_2Se$, 109528-33-8; $(CH_3)_2(CH_3(CH_2)_7)SiCl$, 18162-84-0; Li_2Se, 12136-60-6; $[NH_4]_2[WSe_4]$, 22474-80-2; $[NH_4]_2[WO_4]$, 15855-70-6; $[NEt_4]_2[MoSe_4]$, 114956-91-1; Na_2MoO_4, 7631-95-0; $[AsPh_4]_2[WSe(Se_4)_2]$, 114956-93-3; Se_8, 12597-33-0; $[NEt_4]_2[MoSe(Se_4)_2]$, 114956-94-4; $[AsPh_4]_2[WS(Se_4)_2]$, 113584-94-4; SeS_2, 7488-56-4; $[NEt_4]_2[MoS(Se_4)_2]$, 114956-96-6; $[AsPh_4]_2[WO(Se_4)_2]$, 114956-98-8; $Se_4(N(C_5H_{10}))_2$, 66168-04-5; $[NEt_4]_2[MoO(Se_4)_2]$, 114957-00-5; ^{77}Se, 14681-72-2.

Supplementary Material Available: Listings of anisotropic thermal parameters, hydrogen atom positions, and additional distances and angles for $[NEt_4]_2[MoO(Se_4)_2]$ and $[AsPh_4]_2[WS(Se_4)_2]$ (Tables IS–IIIS and VS–VIIS) (11 pages); listings of $10|F_o|$ vs $10|F_c|$ (Tables IVS and VIIIS) for both complexes (61 pages). Ordering information is given on any current masthead page.

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Synthesis and Magnetic Properties of μ-Organoimido-Bridged Iron(III) Salicylaldimine Compounds. Structure of (μ-*p*-Tolylimido)bis[(*N*,*N'*-ethane-1,2-diylbis(salicylaldiminato))iron(III)] ([Fe(salen)]$_2$N(Tol))

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Received December 29, 1987

The reaction of tetradentate or bidentate Fe(II) salicylaldimine compounds with aryl azides in methylene chloride results in elimination of nitrogen and formation of Fe(III) μ-organoimido-bridged complexes $[Fe(Lig)]_2NR$. Studies of the magnetic susceptibilities of the compounds to 4.2 K show that they possess antiferromagnetic coupling similar to that of the analogous μ-oxo compounds. Mössbauer spectra indicate Fe(III) centers with $S = {}^5/_2$ spin. Crystal data for (μ-*p*-tolylimido)bis[(*N*,*N'*-ethane-1,2-diylbis(salicylaldiminato))iron(III)] ([Fe(salen)]$_2$N(Tol)) ($C_{39}H_{35}Fe_2N_5O_4$): triclinic, $P\bar{1}$, $a = 13.331$ (4) Å, $b = 12.123$ (5) Å, $c = 11.002$ (5) Å, $\alpha = 101.88$ (2)°, $\beta = 96.64$ (3)°, $\gamma = 97.53$ (4)°, $V = 1706$ (1) Å^3, $Z = 2$. The Fe–(μ-N)–Fe angle is 129.6 (6)°.

Introduction

Organoimido complexes of the transition metals are of considerable present interest.[1] Such compounds have been implicated in industrial catalytic processes[2] and enzymatic functions,[3] while other studies have explored their potential for use as reagents or catalysts in the stereospecific transfer of organoimido groups to organic substrates.[4]

The present known range of metal–imido compounds contains relatively few examples from the first transition series, i.e. those elements filling 3d orbitals compared to the heavier 4d and 5d series. Further, there are still few examples known of compounds having chelating ligands attached to the metal in addition to the organoimido group. Dithiocarbamato[5] and porphyrinato[6] ligands have been successfully involved in a variety of such complexes, while Re(V) derivatives containing a variety of salicylaldimines[7] have been reported.

We have previously described[8] the reactions of aryl azides with a Cr(II) porphyrin (Cr(P)) and Fe(II) salicylaldimines (Fe(salR)), which result in the formation of organoimido complexes Cr(NR)(P) and $[Fe(salR)]_2NR$, and in this paper report more fully on the synthesis and properties of the Fe derivatives.

Experimental Section

Materials and Techniques. All manipulations were carried out in dry solvents under purified nitrogen as previously described. Spectra were recorded as follows: infrared, PE 180; mass, PE-RMU-6E. Microanalyses were carried out by the Australian Microanalytical Service and the Australian National University.

The equipment and procedures for magnetic susceptibility and Mössbauer spectral measurements have also been described.[9]

Aryl Azides.[10] Phenyl azide, *p*-tolyl azide, and *p*-chlorophenyl azide were prepared by reaction of the corresponding arenediazonium sulfate with NaN_3 in a two-phase diethyl ether–water mixture and were purified by distillation under pressure or by chromatography on Florisil (60–100 mesh) with ether as eluent. Cyclohexyl azide[11] was prepared from bromocyclohexane. Trimethylsilyl azide was obtained from Aldrich. *Caution*! The aryl azides as a class are reported to detonate if heated to temperatures above 100 °C, while organic azides in general should be treated as potentially liable to detonate, particularly in the presence of heavy metals or acids.

The azides in this work were never subjected to temperatures in excess of 80 °C under any experimental conditions. No instances of explosion were encountered in any aspect of the work.

Fe(III) Complexes. Fe^{II}(salen)py, Fe^{II}(salphen), and Fe^{II}(salmah) (abbreviations for ligands and imido groups used are displayed in Figure 1) were prepared[12] under nitrogen, by reaction between the appropriate, preformed Schiff base and $[Fe(py)_4(SCN)_2]$ in ethanol. The pyridine solvate of Fe(salen) was isolated from the reaction mixture. However, there was no microanalytical or mass spectral evidence for the incorporation of pyridine in the preparation of Fe(salphen) and Fe(salmah). The bidentate complex $Fe(saltol)_2$ was similarly prepared but with anhydrous

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