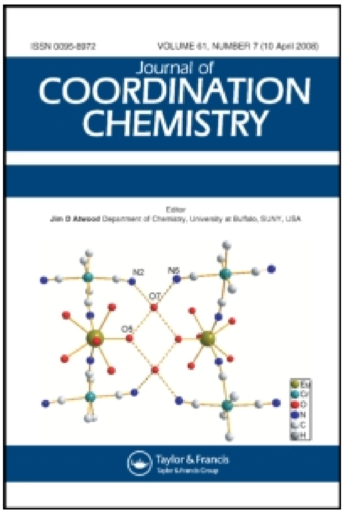

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A NEW FAMILY OF BINUCLEAR MOLYBDENUM(V) AND TUNGSTEN(V) CHALCOHALIDES

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A number of chalcohalide complexes of molybdenum and tungsten having the unusual composition $MS_2X_3(SeX_2)$ (X = Cl, Br) have been synthesized. Their structure has been studied by vibrational spectroscopy, ^{35}Cl and ^{79}Br NQR methods, magnetic measurements and X-ray structure analysis for the bromide compounds. The compounds are dimeric; the metal atoms (d^1) in them are bonded directly by an ordinary bond and bridging S_2 ligands, coordinated perpendicular to the metal–metal bond. The coordination of the SeX_2 (X = Cl, Br) ligands is unusual; the selenium atom, as donor, is bonded to the metal and, as acceptor, to two bridging halogen atoms.

Keywords: Molybdenum(V), tungsten(V), chalcohalides, selenium, synthesis, structure

INTRODUCTION

Among the presently known metal chalcohalides, molybdenum and tungsten compounds seem to be most interesting. A large variety of structure types and properties are characteristic of them, a fact which is due to molybdenum and tungsten being able to exhibit different oxidation states, coordination numbers and to form compounds with metal–metal bonds of different multiplicity, including polynuclear clusters.

During a study of the interaction of molybdenum and tungsten halides and carbonyls with lower sulfur and selenium halides, we have synthesized a family of mixed chalcohalides of the complex composition MS_2SeX_5 (X = Cl, Br).[1–4] Since the compounds obtained have no known analogues, it was thought worth while to elucidate their structures.

Vibrational spectroscopy, ^{35}Cl and ^{79}Br NQR, magnetic susceptibility measurements and X-ray analysis have been used as the main methods with this structural aim in mind.

EXPERIMENTAL

IR spectra were recorded with a Perkin-Elmer 325 spectrophotometer using nujol mulls between polyethylene-protected CsI plates. Raman spectra were recorded using DFS-24 and a He–Ne laser. NQR spectra were recorded with an ISSh-I-13 pulse spectrometer. Magnetic susceptibilities were determined by the standard Faraday method in a helium atmosphere.

Molybdenum and tungsten chalcobromide single crystals were grown during synthesis from stock solutions. Crystal and molecular structure data were collected on an automatic Syntex-P2_1-Fortran four-circle diffractometer with graphite-monochromatized MoK_α radiation. The intensities were collected in the range $4 \leqslant 2\theta \leqslant 45^\circ$ by the $\omega - 2\theta$ scan technique, the speed ranging between 4 and 29.3 deg/min. Absorption corrections were applied, based on azimuthal scans of several reflections. A total of 926 and 1006 independent non-zero reflections were measured for the molybdenum and tungsten compounds respectively, and the data were corrected for Lorenz and polarization effects. Direct methods revealed the positions of the heavy atoms, which were then refined by the full-matrix least-squares method with the "XTL-Syntex" package of programs.

Final anisotropic refinement converged to $R = 0.054$ and 0.071 for the molybdenum and tungsten compounds, respectively. A full description of the structure solution and refinement, together with more structural aspects of this study will be published elsewhere (Koordinatsionnaya Khimiya, 1988, in press).

TABLE I
Vibrational frequencies for the molybdenum and tungsten chalcochlorides.

MoS_2SeCl_5		WS_2SeCl_5		MoS_2Cl_3
IR	R	IR	R	IR
600 m	601 s	590 w	596 m	610 s
395 sh				390 w
385 sh	387 w	375 sh	376 vs	375 w
375 vs	371 vs	365 vs	370 sh	
355 vs	367 sh	340 vs	360 w	345 vs
335 w	348 s		335 s	335 sh
325 s	335 m	325 m	327 s	
305 vs	322 vs	315 s	315 w	310 vs
285 vs	285 s	300 sh	291 m	290 vs
270 m	271 s	290 vs	280 m	265 vs
205 s	235 s	275 sh	264 w	250 sh
	208 vs	205 m	219 m	235 m
			208 s	

TABLE II
Vibrational frequencies for the molybdenum and tungsten chalcobromides.

MoS_2SeBr_5		WS_2SeBr_5		MoS_2Br_3
IR	R	IR	R	IR
585 s	589 m	580 m	584 m	595 s
380 m		365 w		370 m
360 w	343 m		326 m	350 w
335 m	337 w	305 w	312 w	325 m
	328 m	265 sh	260 sh	
275 sh	273 s	255 sh		270 w
255 vs	256 sh	250 vs	252 vs	
250 vs	251 sh		238 vs	240 sh
245 vs	245 vs	220 vs		225 vs
230 vs		205 w		205 vs
210 m				

RESULTS AND DISCUSSION

Vibrational spectra

The observed frequencies were assigned by comparative analysis of spectra and literature data on metal halides and thiohalides and chalcogen halides. Tables I and II list vibrational frequencies for molybdenum and tungsten thiohalides as well as for the thiohalides MoS_2Cl_3 and MoS_2Br_3. The spectra of all the compounds under consideration mainly concern the 200–400 cm^{-1} region. Since in this region there are stretching frequencies of most bonds (metal–halogen, metal–sulfur, selenium–halogen), precise assignment is difficult.

Metal–sulfur stretches occur at 300–390 cm^{-1}; because of their low intensity, they can be assigned without difficulty only when there are no other vibrations present. For instance, only metal–sulfur bond stretches manifest themselves at 300–400 cm^{-1} in the spectra of the chalcobromides (Table II). The spectra of the metal chalcochlorides in this region are much more complex (Table I) and contain strong peaks due to metal–chlorine (300–360 cm^{-1}) and selenium–chlorine stretches (365–390 cm^{-1}). In the spectra of the chalcobromides the metal–bromine stretches manifest themselves at 200–230 cm^{-1} and those of selenium–bromine at 240–275 cm^{-1}. In addition, all the spectra exhibit a band at 580–610 cm^{-1} relating to sulfur–sulfur stretches.

The results obtained indicate that the synthesized compounds have identical structures and are molybdenum(V) and tungsten(V) thiohalide complexes with selenium dihalides, $MS_2X_3(SeX_2)$.

It is noteworthy that the bond stretches of coordinated selenium dichloride and dibromide are somewhat lower than those of the free molecules.[5,6]

It is also interesting to point out some peculiarities of the position of the sulfur–sulfur bond stretching frequency. In the known molybdenum thiochloride MoS_2Cl_3 complexes with tellurium tetrachloride, chloride ion and acetonitrile as well as in molybdenum thiobromide MoS_2Br_3 complexes with bromide ion,[7,8] coordination of these ligands causes some shift of the ν_{S-S} frequency to shorter wavelengths. Coordination of selenium dihalide, on the other hand, causes a shift of this frequency to longer wavelengths (Tables I, II). This may be associated with a redistribution of electron density due to the acceptor properties of the ligand.

The low ν_{S-S} frequency values in the spectra of the tungsten complexes against those for the molybdenum complexes indicate, despite the smaller interatomic S–S distances (below), some contribution of metal–sulfur stretches to the frequency under consideration. The ν_{S-S} frequency decrease in passing from chlorides to bromides is a general trend.

NQR spectra

^{35}Cl and ^{79}Br NQR spectra have been obtained for all synthesized complexes; the resonance frequencies are listed in Table III. The molybdenum and tungsten thioselenohalide spectra are identical and contain a high-frequency doublet and a low-frequency triplet, which agrees with the vibrational spectral data; the doublet relates to the resonance of two halogen atoms bonded to selenium and the triplet to the resonance of three halogen atoms bonded to the metal. However, a strong splitting of the latter is noteworthy. It indicates the halogen atoms bonded to the metal to be chemically nonequivalent. It will be noted that these lines are somewhat higher in frequency than NQR lines in the spectra of simple molybdenum and tungsten halides.[2] This reflects a more covalent character of the metal–halogen bonds in the thioselenohalides and indicates that all the three halogen atoms belong to the inner coordination sphere of the complex. The nature of the nonequivalence of these atoms was established by X-ray structure analysis. As shown below, two of three halogen atoms are at a small distance from the selenium atom; it is to them that the low-frequency NQR doublet corresponds. The splitting is slight and is due to the crystallographic nonequivalence of the corresponding atoms.

TABLE III
Frequencies in the ^{35}Cl and ^{79}Br NQR spectra of the molybdenum and tungsten thioselenohalides, MHz.

$MoS_2Cl_3(SeCl_2)$		$WS_2Cl_3(SeCl_2)$	$MoS_2Br_3(SeBr_2)$		$WS_2Br_3(SeBr_2)$	
77K	296K	77K	77K	296K	77K	296K
35.092	34.515	35.420	276.625	271.743	278.415	273.988
33.470	33.005	33.806	271.221	267.746	273.757	270.516
21.761	21.702	21.182	187.507	185.252	182.260	180.671
16.128	16.022	16.182	135.660	133.656	134.723	133.126
15.840	15.722	15.956	131.878	130.418	132.013	130.812

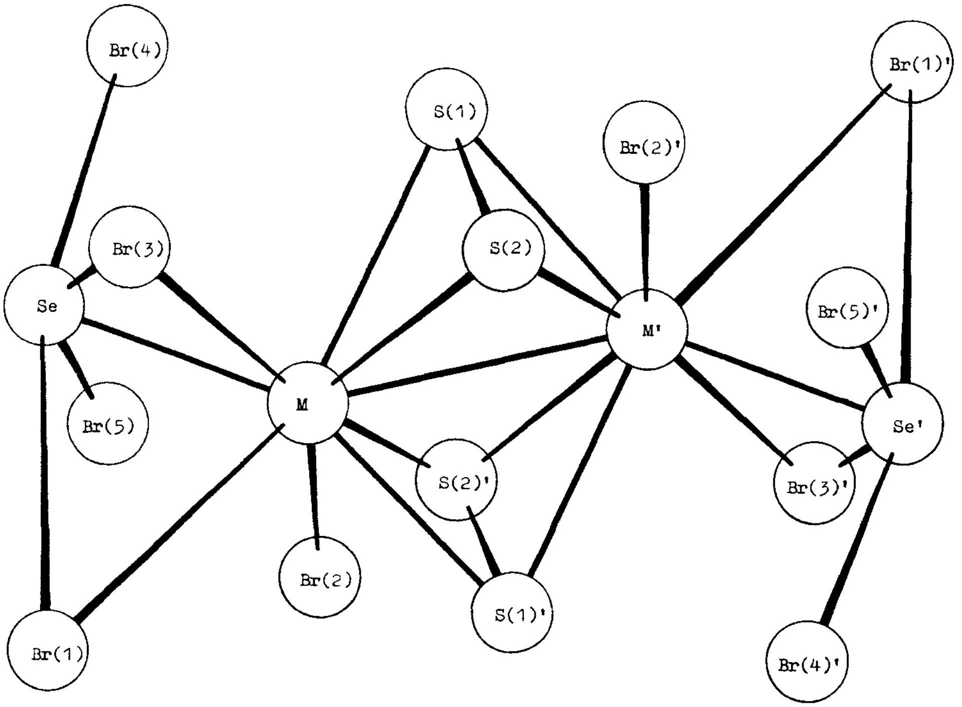

FIGURE 1 Structure of $Mo_2(S_2)_2Br_6(SeBr_2)_2$ and $W_2(S_2)_2Br_6(SeBr_2)_2$.

X-ray structure analysis

The structure studies were performed for the bromide compounds since they formed crystals of the highest quality. The thioselenobromide complexes $MoS_2Br_3(SeBr_2)$ and $WS_2Br_3(SeBr_2)$ are isomorphous and crystallize in the orthorhombic crystal system (space group *Pbca*, $Z = 4$). Lattice parameters (in Å) are $a = 10.744(8)$ and $10.749(2)$, $b = 13.567(8)$ and $13.574(3)$, and $c = 14.000(7)$ and $13.967(2)$ for the two compounds, respectively. The calculated density (4.16 and 4.74 g cm^{-3}) and the experimentally found density (4.06 and 4.67 g cm^{-3}) are in satisfactory agreement.

The structures of both compounds are of discrete units (the distances between the units are over 3.6Å) and consist of the centrosymmetric dimers $M_2(S_2)_2Br_6(SeBr_2)_2$ (Fig. 1).

The main interatomic distances are listed in Table IV and the valence angles in Table V.

TABLE IV
Interatomic distances in the chalcobromide complexes of molybdenum and tungsten, Å.

	$MoS_2Br_3(SeBr_2)$	$WS_2Br_3(SeBr_2)$
$M - M$	2.801(3)	2.792(2)
$M - Br_1$	2.576(3)	2.575(4)
$M - Br_2$	2.609(3)	2.594(5)
$M - Br_3$	2.576(3)	2.565(4)
$M - S_1$	2.413(5)	2.428(9)
$M - S_1'$	2.435(6)	2.431(10)
$M - S_2$	2.422(6)	2.414(10)
$M - S_2'$	2.437(6)	2.427(10)
$M - Se$	2.685(3)	2.690(4)
$S_1 - S_2$	2.026(8)	1.985(13)
$Se - Br_1$	2.857(3)	2.853(4)
$Se - Br_3$	2.849(3)	2.845(5)
$Se - Br_4$	2.349(4)	2.338(6)
$Se - Br_5$	2.354(4)	2.349(5)

TABLE V
Valence angles in the molybdenum and tungsten chalcobromide complexes, degrees.

	$MoS_2Br_3(SeBr_2)$	$WS_2Br_3(SeBr_2)$
S_1MS_1'	109.42(20)	109.60(31)
S_2MS_2'	109.62(19)	109.90(25)
MS_1M'	70.38(16)	70.13(25)
MS_2M'	70.58(16)	70.43(27)
Br_1SeBr_3	76.45(9)	76.10(15)
Br_1SeBr_4	166.83(13)	166.70(22)
Br_1SeBr_5	92.26(11)	92.37(19)
Br_3SeBr_4	94.24(11)	94.43(19)
Br_3SeBr_5	165.26(13)	164.74(23)
Br_4SeBr_5	95.20(13)	95.03(22)
$MSeBr_1$	55.27(8)	55.90(12)
$MSeBr_3$	55.38(8)	55.20(12)
$MSeBr_4$	111.75(12)	111.46(19)
$MSeBr_5$	110.33(12)	109.98(19)

The metal–metal distances are close to those of metallic molybdenum (2.78Å) and tungsten (2.80Å). Molybdenum(V) and tungsten(V) have an electronic configuration d^1, and bond may exist between the metal atoms in dimer molecules. The diamagnetism of the compounds and the form of the $M_2(S_2)_2$ polyhedron (MSM′ angles $<90°$ and SMS′ angles $>90°$) indicate unambiguously (as well as the interatomic distances) its presence.

The formation of dimeric complexes is also associated with the coordination of disulfide groups by neighbouring atoms. Owing to this, molybdenum and tungsten have coordination number 9. Three bromine atoms are directly bonded to the metal atom in the molecule, two of them also lying close to the selenium atom- at a distance that is within chemical bonding limits (the Se–μ–Br distance in the known anion $Se_2Br_6^{2-}$ is 2.887Å).[9] As was pointed out above, NQR spectra argue unambiguously in favour of chemical bonding.

Other chloride complexes of many metals with sulfur and selenium dichlorides are known. However, such a type of coordination as reported here is not observed and only concerns direct chalcogen to metal bonding. In terms of the valence bond approach the observed structure of the complexes may be accounted for as follows. When the $SeBr_2$ (or $SeCl_2$) molecule is coordinated, the selenium atom as donor is bonded to the metal, and as acceptor, to two bridging bromine atoms (two electron pairs in the vacant 4d-orbitals). As a result, six electron pairs belong to the selenium, five of which are bonding and one nonbonding. The valence angles and bond lengths (Tables IV, V) allow the conclusion to be drawn that the selenium coordination polyhedron is a distorted tetragonal pyramid. In terms of this the bonds in the polyhedron under consideration may be assumed to be formed by sp^3d^2 hybrid selenium orbitals as in the known $SeBr_4^{2-}$ and $Se_2Br_6^{2-}$ anions, which have a planar structure.[9]

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