Reductive Addition at the $W_3S_4^{4+}$ Core by Sn^{2+} or an Unusual Supramolecular System: A Synergetic Reaction Leading to the Host Guest Compound $(Me_2NH_2)_6[(SCN)_9W_3S_4SnCl_3] \cdot 0.5H_2O$

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The mixed-metal cluster compound $(Me_2NH_2)_6[(SCN)_9W_3S_4SnCl_3] \cdot 0.5H_2O$ (**1**) with the cubane-type $[W_3(\mu_3\text{-}S)_4Sn]$ core has been prepared by reacting $W_3S_4^{4+}$ in aqueous HCl solution with $SnCl_2 \cdot 2H_2O$ in the presence of Me_2NH_2Cl and $NaSCN$. **1** was characterized by X-ray crystallography and by ^{119}Sn Mössbauer, photoelectron, and electronic absorption spectroscopy. Crystals of **1** are monoclinic, of space group $C2/c$, with $a = 42.792(10)$ Å, $b = 11.988(2)$ Å, $c = 21.725(3)$ Å, $\beta = 95.24(2)°$, and $Z = 8$. The structure was refined by full-matrix least-squares techniques to $R = 0.069$ and $R_w = 0.071$ for 7690 reflections with $F > 4\sigma(F)$. The formation of **1** is due to a synergetic effect: The affinity of the W_3S_4 ligand for cations like Sn^{2+} is increased as its electron-donor strength is increased by the reducing cation itself. An alternative description would be to insert a plug formed mainly from the Sn 5s level into a socket formed from acceptor levels localized on the W_3 triangle, which is equivalent to a novel type of host guest interactions.

Introduction

The three coordinatively unsaturated μ-sulfur atoms in the incomplete cubane-type (cuboidal) clusters $[M_3(\mu_3\text{-}S)(\mu_2\text{-}S)_3]$ (M = Mo, Fe) offer the possibility of coordinating transition and post-transition metal atoms whereby cubane-type mixed-metal clusters with $[M_3(\mu_3\text{-}S)_4M']$ cores can be formed.[1,2] The cuboidal cluster formally acts as ligand for M'. It should be noted that the chemistry of mixed-metal cluster species with M_3S_4M' cores is of relevance to several interdisciplinary problems.[1–4] The above mentioned type of reaction is important, for instance, for understanding the formation of heterometal clusters in proteins: incubation of proteins containing reduced $[Fe_3S_4]^{0,1-}$ clusters with salts of transition and post-transition elements (M' = Co, Ni, Zn, Cd) leads to several protein-bound cubane-type species $[Fe_3(\mu_3\text{-}S)_4M']$.[5] An elegant method for the synthesis of such clusters is the heterometal atom M incorporation into the aqua ion

$[Mo_3S_4(H_2O)_9]^{4+}$(M = Fe, Co, Ni, Pd, Cu, Hg, In, Sn). In this case, the reaction can be regarded as the reductive addition of a metal center to the $Mo^{IV}_3S_4^{4+}$ core.[1,6]

The chemistry of the triangular $W_3S_4^{4+}$ clusters is far less developed than that of the analogous species of molybdenum[1,7] and only a $W_3S_4Cu^+$ cubane-type cluster has been reported until now.[8] Note that $Mo_3S_4^{4+}$ clusters are more easily reduced than the tungsten analogues, which leads to stronger interactions in the context discussed below.[9]

We describe here the synthesis, characterization, ^{119}Sn Mössbauer spectrum, photoelectron spectra, and X-ray structure analysis of a new cubane-type mixed-metal cluster compound $(Me_2NH_2)_6[(SCN)_9W_3S_4SnCl_3] \cdot 0.5H_2O$ (**1**) with a W_3S_4Sn core, which is formed according to an interesting synergetic reaction pathway. Because of the unexpected complexity and novelty of the interaction between two anions which are stable themselves but showing weak interactions, several models and alternative views will be presented.

Experimental Section

All experiments were carried out in air. $(NH_4)_2[W_3S_4(S_4)_3(NH_3)_3] \cdot H_2O$ was prepared according to a previously published procedure.[7e]

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(8) (a) Zhan, H.-Q.; Zheng, Y.-F.; Wu, X.-T.; Lu, J.-X. *Inorg. Chim. Acta* **1989**, *156*, 277. (b) Zhan, H.-Q.; Zheng, Y.-F.; Wu, X.-T.; Lu, J.-X. *Jiegon Huaxue* **1988**, *7*, 157. In ref 20 of their paper, Shibahara et al.[7h] claim the preparation of a W_3S_4Sn cluster; however, no details were given until now.
(9) For example, the clusters $[Mo_3S_4(Hnta)_3]^{n-}$ ($n = 2–4$) are more easily reduced (0.48, 0.33, and 0.49 V, respectively) than the tungsten analogues[7h].

Table 1. Crystallographic Data for
$(Me_2NH_2)_6[(SCN)_9W_3S_4SnCl_3]\cdot 0.5H_2O$ (1)

empirical formula	$C_{21}H_{49}Cl_3N_{15}O_{0.5}S_{13}SnW_3$
color	brown
crystal size	$0.60 \times 0.30 \times 0.10$ mm³
crystal system	monoclinic
space group	$C2/c$
unit cell dimens	$a = 42.792(10)$ Å
	$b = 11.988(2)$ Å
	$c = 21.725(3)$ Å
	$\beta = 95.24(2)°$
volume	11 098(3) Å³
Z	8
formula weight	1713.1
density (calcd)	2.05 g cm⁻³
abs coeff	7.43 mm⁻¹
transm coeff	0.055–0.154
$F(000)$	6520
$R/R_w{}^a$	0.069/0.071

^{a} $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{0.5}$; $w^{-1} = \sigma^2(F) + 0.0002F^2$.

Preparation of $(Me_2NH_2)_6[(SCN)_9W_3S_4SnCl_3]\cdot 0.5H_2O$ (1). After a mixture of $(NH_4)_2[W_3S_4(S_4)_3(NH_3)_3]\cdot H_2O$ (1.00 g) and 10 mL of concentrated hydrochloric acid was boiled for 20 min, the resulting solution of $W_3S_4^{4+}$ was filtered off and $SnCl_2\cdot 2H_2O$ (0.50 g) was added to the filtrate. The dark-red solution was stirred for 3 min, and H_2O (50 mL), NaSCN (2.0 g), and Me_2NH_2Cl (2.0 g) were added. After the solution was kept at ambient temperature for 2 days, the dark brown precipitated crystals were isolated by filtration and dried in air. Yield: 1.16 g (79%).[10] Anal. Calcd for $C_{21}H_{49}Cl_3N_{15}O_{0.5}S_{13}SnW_3$: C, 14.72; H, 2.88; N, 12.26; Cl, 6.21; S, 24.33. Found: C, 14.56; H, 2.90; N, 11.95; Cl, 6.41; S, 24.2. IR (as KBr pellet or in polyethylene): ν(CN) 2102 (vs), ν(CS) 810 (m), δ(NCS)/ν(WN)/ν(SnCl) 474 (w), 454 (w), 416 (w), 404 (sh), 337 (w), 273 (sh), 257 (sh), 241 (s), 215 (s) cm⁻¹. FT-Raman ($\lambda_e = 1060$ nm): 486 (w), 422 (sh), 405 (s), 352 (w), 339 (w), 284 (s), 260 (s), 243 (s), 222 (m) cm⁻¹.

Photoelectron Spectroscopy. Core level and valence band photoelectron spectra were recorded with a Leybold-Heraeus LHS-10 spectrometer with Mg Kα (XPS) and He I and He II (UPS) radiation. As a consequence of the insulating nature of the sample, a surface charging of several volts occurred. For energy calibration of the XP spectra the C 1s peak was used, which is composed of contributions from the SCN and methyl groups and from the internal carbon contamination of the spectrometer. The experimental C 1s signal decomposed into two components. The component at lower binding energy is assigned to the internal carbon contamination ($E_b = 285$ eV), which is confirmed by the diminution of its intensity after scraping the sample surface. The other component at 286.7 eV is the superposition of the two kinds of intrinsic C atoms. During the acquisition of the UP spectra, the sample was flooded by low-energy electrons. For energy calibration, the UP spectra were shifted so that the top of the valence bands of XP and UP spectra coincided. The uncertainty in the E_b values due to the calibration procedure is about 0.5 eV. In order to minimize disturbances due to the loss of crystal water, the spectra were recorded at 77 K.

Structure Determination. Diffraction data for the title compound were collected on a Siemens R3m/V diffractometer using graphite-monochromatized Mo Kα radiation ($\lambda = 0.710$ 73 Å); 2θ limits = 4.0–52.0°; $R = 0.069$ and $R_w = 0.071$ for 7690 reflections ($F > 4\sigma(F)$). The structure was solved by direct methods (Siemens SHELXTL-PLUS (VMS))[11] and refined by full-matrix least-squares procedures. Crystal data for 1 are summarized in Table 1, and the atomic coordinates and selected interatomic distances for the $[(SCN)_9W_3S_4SnCl_3]^{6-}$ ion in 1 are listed in Tables 2 and 3, respectively.

¹¹⁹Sn Mössbauer Spectroscopy. The spectrum of a solid absorber sample was recorded; apparatus and procedures have been reported elsewhere.[12]

Results and Discussion

The incomplete cubane-type cluster ion $[W_3(\mu_3\text{-}S)(\mu_2\text{-}S)_3]^{4+}$ but also the corresponding intact NCS cluster react in aqueous

(10) In order to ensure product homogeneity, the X-ray powder diffraction diagram of the product was obtained and found to be identical with the one calculated from the single-crystal data.
(11) Siemens Analytical Instruments, SHELXTL-PLUS, Revision 4.11, 1990.
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Table 2. Atomic Coordinates and Equivalent Isotropic Displacement Coefficients for $[(SCN)_9W_3S_4SnCl_3]^{6-}$ in 1

atom	x	y	z	$U(eq)^a$ (Å² × 10²)
W(1)	0.1228(1)	0.8035(1)	0.0114(1)	3.8(1)
W(2)	0.0856(1)	0.8665(1)	−0.0919(1)	3.9(1)
W(3)	0.1384(1)	0.9867(1)	−0.0539(1)	4.1(1)
Sn	0.1599(1)	0.7259(1)	−0.1380(1)	5.8(1)
Cl(1)	0.1376(2)	0.6416(6)	−0.2373(3)	16.4(6)
Cl(2)	0.2070(2)	0.7974(6)	−0.1857(5)	17.0(5)
Cl(3)	0.1867(1)	0.5432(4)	−0.1120(3)	8.3(2)
S(1)	0.1488(2)	0.9739(2)	0.2144(3)	9.8(3)
S(2)	0.1766(2)	0.5172(7)	0.1408(4)	15.4(4)
S(3)	0.0433(1)	0.6411(5)	0.1348(3)	8.2(2)
S(4)	−0.0159(1)	0.7659(5)	−0.0190(3)	10.2(3)
S(5)	0.0429(2)	0.7056(7)	−0.2911(3)	12.8(3)
S(6)	0.0366(1)	1.2044(4)	−0.1848(3)	7.5(2)
S(7)	0.1089(2)	1.3794(4)	−0.0799(3)	9.1(2)
S(8)	0.2297(1)	1.1429(5)	−0.1493(3)	9.6(3)
S(9)	0.1950(2)	1.2034(7)	0.1133(4)	15.9(4)
S(10)	0.1079(1)	0.6895(3)	−0.0736(2)	4.6(1)
S(11)	0.1256(1)	0.9159(3)	−0.1527(2)	4.7(1)
S(12)	0.1712(1)	0.8355(3)	−0.0273(2)	4.5(1)
S(13)	0.0932(1)	0.9683(3)	0.0011(2)	4.1(1)
N(1)	0.1373(3)	0.8694(11)	0.1003(6)	5.6(5)
N(2)	0.1463(3)	0.6596(11)	0.0532(7)	5.7(5)
N(3)	0.0851(3)	0.7382(11)	0.0605(6)	5.3(5)
N(4)	0.0415(3)	0.8189(11)	−0.0601(6)	5.2(5)
N(5)	0.0650(3)	0.7931(10)	−0.1772(7)	5.2(5)
N(6)	0.0604(3)	1.0086(10)	−0.1255(7)	5.2(5)
N(7)	0.1204(3)	1.1469(11)	−0.0770(7)	6.1(5)
N(8)	0.1780(3)	1.0559(11)	−0.0945(6)	5.3(5)
N(9)	0.1606(3)	1.0754(11)	0.0236(7)	5.4(5)
C(1)	0.1430(4)	0.9131(15)	0.1469(8)	5.9(7)
C(2)	0.1590(5)	0.6019(15)	0.0903(9)	6.7(7)
C(3)	0.0673(4)	0.6967(13)	0.0911(7)	4.9(6)
C(4)	0.0172(4)	0.7967(14)	−0.0436(8)	5.8(6)
C(5)	0.0553(5)	0.7537(14)	−0.2256(9)	6.5(7)
C(6)	0.0508(4)	1.0934(15)	−0.1508(7)	5.1(6)
C(7)	0.1160(4)	1.2451(14)	−0.0767(9)	6.4(7)
C(8)	0.1989(4)	1.0928(15)	−0.1166(8)	6.0(7)
C(9)	0.1745(4)	1.1310(14)	0.0606(10)	7.1(8)

^{a} Equivalent isotropic U values defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 3. Selected Interatomic Distances (Å) for $[(SCN)_9W_3S_4SnCl_3]^{6-}$ in 1

W(1)–W(2)	2.735(1)	W(1)–W(3)	2.730(1)
W(1)–S(10)	2.338(4)	W(1)–S(12)	2.337(4)
W(1)–S(13)	2.346(4)	W(1)–N(1)	2.126(13)
W(1)–N(2)	2.156(13)	W(1)–N(3)	2.161(14)
W(2)–W(3)	2.741(1)	W(2)–S(10)	2.345(4)
W(2)–S(11)	2.330(4)	W(2)–S(13)	2.357(4)
W(2)–N(4)	2.146(14)	W(2)–N(5)	2.167(13)
W(2)–N(6)	2.112(12)	W(3)–S(11)	2.327(4)
W(3)–S(12)	2.332(4)	W(3)–S(13)	2.373(4)
W(3)–N(7)	2.113(13)	W(3)–N(8)	2.149(14)
W(3)–N(9)	2.139(13)	Sn–Cl(1)	2.492(7)
Sn–Cl(2)	2.502(9)	Sn–Cl(3)	2.512(5)
Sn–S(10)	2.768(5)	Sn–S(11)	2.713(4)
Sn–S(12)	2.743(4)		

HCl solution at room temperature with $SnCl_2\cdot 2H_2O$. The title compound $(Me_2NH_2)_6[(SCN)_9W_3S_4SnCl_3]\cdot 0.5H_2O$ (1) could be isolated in high yield from 2 M aqueous HCl solution in the presence of NaSCN and Me_2NH_2Cl.

$$[W_3(\mu_3\text{-}S)(\mu_2\text{-}S)_3]^{4+} + Sn^{2+} + 9SCN^- + 3Cl^- \rightarrow$$
$$[(SCN)_9W_3(\mu_3\text{-}S)_4SnCl_3]^{6-}$$
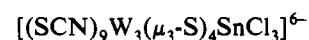
This corresponds to a very simple method, as no anaerobic technique and/or no chromatographical procedure is required (see ref 6). It is interesting to note that the chloride ligand selectively attaches itself to the Sn and the thiocyanate to the W centers *via* N coordination. This kind of selectivity might be explained in terms of the slightly different "hardnesses" of the metal centers.
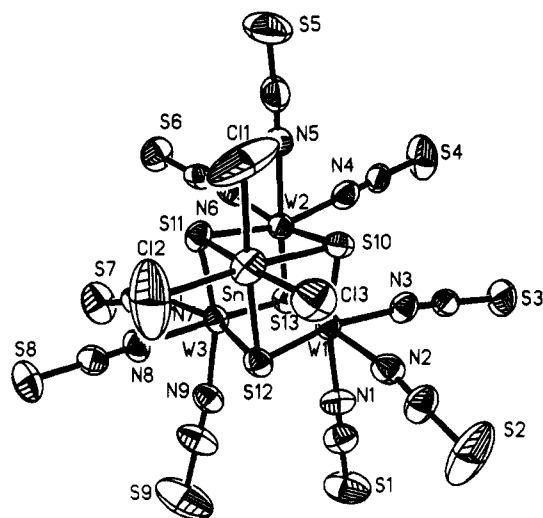
Figure 1. Perspective view of the structure of the [(SCN)₉W₃S₄SnCl₃]⁶⁻ anion in **1** without distinguishing between stronger (Sn–Cl) and weaker (Sn–S) interactions.

Figure 2. ¹¹⁹Sn Mössbauer spectrum of (Me₂NH₂)₆[(SCN)₉W₃S₄-SnCl₃]·0.5H₂O at 77.3 K: Experimental data, +++; computer-fitted Lorentzian line shape, - - -. Sample thickness: 0.51 mg of ¹¹⁹Sn/cm². Mössbauer parameters: isomer shift, δ = 2.44 mm s⁻¹ (relative to room temperature CaSnO₃); nuclear quadrupole splitting, ΔE = 0.00; full width at half-height of the resonant peak, Γ = 1.21 mm s⁻¹.

Under similar experimental conditions, germanium cluster compounds with W₃S₄Ge cores could also be obtained from W₃S₄⁴⁺ and Ge²⁺.[13] In this context, it is worth mentioning that Pb²⁺, as expected, does not react with the W₃S₄⁴⁺ aqua cluster or [W₃S₄(NCS)₉]⁵⁻ in CH₃CN since Pb²⁺ is not as strong a reducing agent as Sn²⁺ or Ge²⁺. **1** is diamagnetic and dissolves in H₂O as well as in some organic solvents (methanol, acetone, acetonitrile, DMF). The solutions are stable toward air oxidation.

The X-ray crystal structure analysis of **1** proved the abundance of the heterometal cubane-type W₃S₄Sn core. The structure of the anion [(SCN)₉W₃S₄SnCl₃]⁶⁻ is shown in Figure 1. The reductive addition of Sn²⁺ to the [W₃S₄(NCS)₉]⁵⁻ cluster does not essentially change the geometry of the W₃S₄ fragment. The W–W bonds in **1** (2.730(1)–2.741(1) Å) are for instance (slightly) shorter than those in [W₃S₄(NCS)₉]⁵⁻ (2.760(1)–2.764(1) Å)⁷ʰ. This would not be expected in case of the simple model of an electron configuration [W₃]⁸ being discussed below.

Each metal atom is octahedrally coordinated, either by three sulfur and three nitrogen atoms (in the case of tungsten) or by three sulfur and three chlorine atoms (in the case of tin). Therefore, **1** represents the uncommon example of an M₃S₄M' type cluster in which all four metal atoms have similar octahedral coordinations.[14] The W–Sn distances (3.778(1)–3.856(1) Å) and the Sn–S distances (2.713(4)–2.768(5) Å) are rather long, and SSnS angles (73.6(1)–75.6(1)°), rather small. This implies little or almost no W–Sn interaction in **1** and a weak Sn–S bonding. The Sn–Cl distances (2.492(7)–2.512(5) Å) are shorter than the representative bond lengths reported for Snᴵᴵ complexes (for instance, in (NH₄)₂[SnCl₃]Cl·H₂O)[15] but longer than the bond lengths reported for Snᴵⱽ species (in SnCl₆²⁻ salts the tin atoms have nearly octahedral symmetry with bond lengths about 2.40–2.44 Å[16]). Simple bond valence sum calculations also show that the formal oxidation state of Sn is between II and IV.

The ¹¹⁹Sn Mössbauer spectrum and related parameters (see Figure 2 and its caption) give further information regarding the environment and bonding at the tin atom. A one-line spectrum clearly occurs according to the narrowness of the Γ parameter
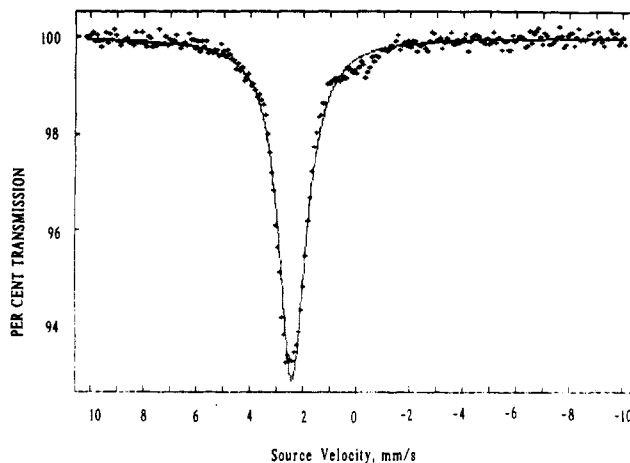
(see e.g. ref 17, Table 17), consequently leading to a lack of nuclear quadrupole splitting (ΔE = 0.00), which is perfectly in accordance with the molecular structure determined here. In fact, the arrangement of the ligand atoms at the Sn center, shown in Figure 1, involves the approximate equality of the principal components of the electric field gradient tensor at the Sn nucleus: $V_{xx} \approx V_{yy} \approx V_{zz}$,[17] which corresponds to ΔE = 0 according to point charge model calculations. (ΔE = 0 corresponds to an exact regular octahedral environment of tin.) The measured isomer shift is larger than those reported for Snᴵⱽ complexes but less than those reported for Snᴵᴵ complexes with Sn–S and/or Sn–Cl bonds.[17,18]

In order to obtain more detailed information about the electronic structure, **1** was investigated also by photoelectron spectroscopy. In agreement with the results from the structure determination and from Mössbauer spectroscopy, the Sn 3d and W 4f core level spectra consist of a single line for each spin–orbit component. The binding energy E_b = 487.1(5) eV of the Sn 3d electrons, however, does not allow an assignment of an oxidation state, as the variation of E_b with oxidation state is not significant for Sn compounds.[19] The E_b value of 33.4(5) eV for the W 4f₇/₂ signal is typical for W oxidation states in the range of III–IV,[20] in agreement with the considerations concerning chemical bonding in the W₃ cluster (see below).

In Figure 3 the valence band spectra of **1** are depicted. From the atomic photoionization cross sections[21] and the sample stoichiometry, it is seen that the XP valence band spectrum is dominated by a photoemission from W 5d and S 3p orbitals with relative intensity weights of 60% and 40%, respectively, besides contributions from Cl 3p, C 2s, and N 2s orbitals. The UP valence band spectra are mainly due to photoemission from N 2p (47%/36%) and C 2p (29%/28%) orbitals, besides contributions from W 5d (18%/18%) and S 3p (6%/14%) orbitals. The respective relative intensity weights for He II and He I spectra as estimated from the photoionization cross sections are given in parentheses. Comparison with the experimental spectra shows that the highest occupied states, the relative photoemission intensity of which is much higher in the XP than in the UP spectra, are mainly of W

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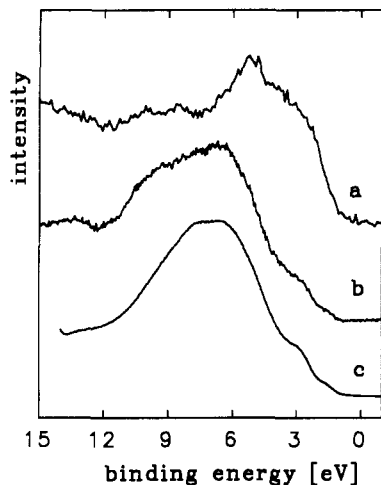(21) Yeh, J. J.; Lindau, I. *At. Data Nucl. Data Tables* **1985**, *32*, 1.

Figure 3. Valence band spectra of **1**. The sample was excited with (a) MgKα (1253.6 eV), (b) He II (40.8 eV), and (c) He I (21.2 eV) radiation.

Figure 4. Results of the extended Hückel MO calculations for (a) the LUMO of a $W_3S_4^{4+}$ fragment and (b) the HOMO of the $SnCl_3^-$ anion. The size of the lobes indicates the relative localization of the corresponding levels.

5d character. The main contribution from the S 3p orbitals occurs at higher binding energies and is reasonably attributed to the peak at 5 eV in the XP spectrum although there might be a certain overlap between W 5d and S 3p orbitals. The UP spectra show that the center of the N 2p and C 2p orbitals is below the center of the cluster orbitals. Unfortunately possible contributions from Sn 5s and Sn 5p orbitals to the photoemission intensity are too small to be identified in the XP or UP spectra. The spectroscopic results are in complete accordance with the results of our MO calculations (see below).

A formal reductive addition of an Sn^{2+} ion to the $W_3S_4^{4+}$ core is expected to change the electronic spectrum of **1** [in CH_3CN; λ_{max}, nm (ϵ M^{-1} cm^{-1}): 345 sh, 418 (6430), 564 (1440)] considerably from that of the $[W_3S_4(NCS)_9]^{5-}$ ion in the visible region [in CH_3CN: 625(720)][7e] according to the results given below which were based on the MO scheme for M_3 cluster moieties. (Characteristically different bands were reported for the electronic spectrum of the one-electron-reduced species of $[W_3S_4(Hnta)_3]^{2-}$)[7h].

A species like $[W_3S_4(NCS)_9]^{5-}$ belongs within our classification of trinuclear clusters of the early transition elements to the B_1 type[22] ($[M_3(\mu_3-X)(\mu_2-Y)_3L_9]$ with an electron configuration $[M]^6$ or $(1a_1)^2(1e)^4(2a_1)^0(2e)^0$). Calculations of the orbital energies for clusters of type B_1 lead within the Cotton–Haas model[23] to an MO scheme with three bonding MOs ($1a_1$ and $1e$) and one weakly bonding or nonbonding one ($2a_1$). From the MO scheme it is understandable that the clusters may exist with six (most common clusters which satisfy the 18-electron rule), seven, or eight electrons in the metal cluster system whereby those with seven electrons should be paramagnetic. (Electronic transitions predominantly occurring within the M_3 fragments are symmetry allowed and should have higher intensities than the corresponding d–d transitions of mononuclear species; ligand → metal and metal → ligand charge-transfer transitions are normally expected only at higher energies.) For $[M_3]^6$ clusters the assignment $1e → 2a_1$ for the longest wavelength transitions should be approximately correct.[22]

It is especially interesting, that the anion of the title compound still has C_{3v} symmetry and contains the $[W_3S_4(SCN)_9]$ unit as an intact fragment or as a ligand. Therefore, the electronic structure of the anion of **1** could be—within the same symmetry framework—related to that of the starting cluster ion $[W_3S_4(NCS)_9]^{5-}$ (especially taking into consideration that the perturbation of the W_3 orbitals is weak; see the comparison of the corresponding distances). In the *formally* complete two-
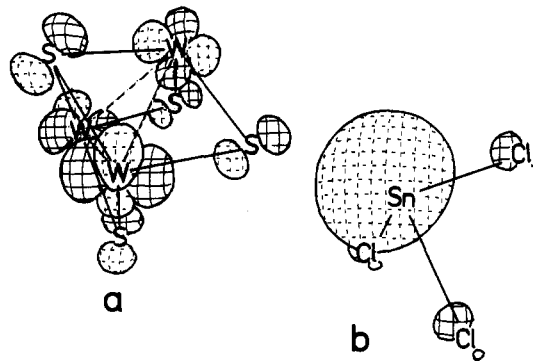
electron-reduced $[W_3]^8$ cluster (see below) the $1e → 2a_1$ transition of the $[W_3]^6$ cluster is now no longer possible and the longest wavelength band at 564 nm should (approximately) be assigned to a $2a_1 → 2e$ transition. This assignment could formally be regarded as being consistent with the structure of the highest occupied states seen in the UP spectra. Within this model it would be reasonable to attribute the larger shoulder around 2.7 eV to a photoemission from the doubly degenerate $1e$ orbitals and the small feature at lower binding energy to photoemission from the $2a_1$ orbital of the "reduced" cluster. Contributions from the $1a_1$ orbitals are not resolved in the UP spectra but contribute presumably to the higher binding energy part of the main peak in the XP spectrum.

The formation of the title compound shows that the incomplete cubane-type cluster $[W_3(\mu_3-S)(\mu_2-S)_3]^{4+}$ can be used as a reactive fragment, for instance for the generation of a cubane-type cluster by addition of another metal atom. Reduction of, or better partial electron transfer to, the $W_3S_4^{4+}$ core by Sn^{2+} even increases the nucleophilicity (electron density) of the three coordinatively unsaturated μ_2-S atoms. ($[W_3S_4(H_2O)_9]^{4+}$ and $[W_3S_4(NCS)_9]^{5-}$ do not react with Sn^{4+}!) In this context, it is important to note that therefore the formation of the title compound is due to a synergetic effect: The affinity of the W_3S_4 fragment (ligand) for cations like Sn^{2+} is increased as its electron-donor strength is increased by the reducing cation itself.[24,25] (This property is associated with the fact that the $W_3S_4^{4+}$ ligand has a vacant $2a_1$ orbital (in addition to μ_2-S lone pairs) which can accept electrons like a typical π-acceptor ligand, thereby increasing the σ-donor bond strength.) Correspondingly, the Mössbauer spectrum can be explained by the statement that the W_3S_4 fragment behaves like a noninnocent ligand, causing the oxidation state of Sn to be between II and IV (correspondingly the formal oxidation state of W is between III and IV).

Furthermore we have studied the reductive addition of $SnCl_3^-$ to the W_3 complex by extended Hückel MO calculations.[26] The

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(24) Recently Holm also proposed that the Fe_3S_4 unit, for instance could be considered as a quasi-rigid cluster ligand: Ciurli, S.; Holm, R. H. *Inorg. Chem.* **1991**, *30*, 743. See also ref 2.

(25) The chemistry of the trinuclear metal sulfur clusters showed an "explosive" interest after the first relevant species were published (see review in ref 22). Important aspects are their high tendencies to form in solution and even in amorphous substances in the case of early transition elements with intermediate oxidation states (Müller, A.; Fedin, V.; Hegetschweiler, K.; Amrein, W. *J. Chem. Soc., Chem. Commun.* **1992**, 1795. Müller, A.; Diemann, E.; Krickemeyer, E.; Walberg, H.-J.; Bögge, H.; Armatage, A. *Eur. J. Solid State Inorg. Chem.* **1993**, *30*, 565) and their reactivities and ligand properties discussed here. This is also valid for their electrochemistry (Wieghardt, K.; Herrmann, W.; Müller, A.; Eltzner, W.; Zimmermann, M. *Z. Naturforsch.* **1984**, *39B*, 876).

(26) SCCC type calculations,[27] using a modified version[28] of the EHT-SPD program.[29] We used single-ζ functions and H_{ii}'s from ref 30 and (for W) from ref 31. For charge iteration on W, we employed the VOIP curves as given in ref 32. The geometrical data were taken from the cited references and from our structure determination.

HOMO of $SnCl_3^-$ originates mainly from the Sn 5s level. It is depicted in Figure 4b and is clearly higher in energy than the LUMOs of the W_3 complex which are shown in Figure 4a. The latter are localized mainly on the W_3 triangle. The reaction may then be described as "inserting a plug into a socket", resulting in an electron transfer from the former to the latter. Since the accepting level is stabilized by the addition of the tin anion, a population of the new HOMO should also result in a slight decrease of the W–W bond length, as observed experimentally. An especially interesting result of the present study is the possibility to consider the cluster anion of **1** as a novel type of inorganic host (*anionic* (!) $[W_3S_4(SCN)_9]^{5-}$)–guest (*anionic* (!) $SnCl_3^-$) system which is justified because of the weak interaction between two anions, which are themselves stable and complementary (plug/ socket).

Inverted $M_4S_3 = [M_4(\mu_3\text{-}S)_3]$ clusters[2,4a] also belong to the group of cuboidal species (inverted population of metal and sulfur sites). Though they cannot act as ligands like the M_3S_4 units (there are no μ_2-S atoms), the analogue M_2S_3M' units with an incomplete cube (for instance $[O{=}M'(\mu_3\text{-}S)(\mu_2\text{-}S)_2M_2(PPh_3)_3]$ ($M' = $ Mo, W; $M = $ Cu, Ag)) again have coordinatively unsaturated μ_2-S centers and can coordinate to metal centers like the M_3S_4 fragments.[4b-d] This type of behavior seems to be of general importance for comparable systems with μ_2-S sites in proteins, too.

Supplementary Material Available: Tables of data collection parameters, atom coordinates, bond lengths, bond angles, and anisotropic displacement coefficients for **1** (7 pages). Ordering information is given on any current masthead page.

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