Structure and Vibrational Spectrum of Bis(tetrathiotungstato)zincate(II), [Zn(WS₄)₂]²⁻

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The crystal and molecular structures of tetraphenylphosphonium bis(tetrathiotungstato)zincate, $[P(C_6H_5)_4]_2[Zn(WS_4)_2]$, were determined from single-crystal x-ray diffractometer data. The diffraction pattern of the tetragonal compound shows strong and sharp reflections of a substructure cell (space group $I\bar{4}$, with $a = 13.292$ (5) Å, $c = 6.890$ (2) Å, $V = 1217.3$ Å³, $Z = 1$, $d_{exptl} = 1.88$ (2) g/cm³, $d_{calcd} = 1.866$ g/cm³) besides weak and diffuse superstructure reflections ($I\bar{4}$, $a' = a + b$, $c' = 2c$, $Z = 4$), caused by a partially disordered arrangement of the anions. Least-squares refinement of 720 independent substructure reflections gave a final R factor of 0.044; the nature of the superstructure was derived from 1009 diffuse reflections. The structure consists of isolated $[Zn(WS_4)_2]^{2-}$ and tetraphenylphosphonium ions. In the complex anion the central Zn is coordinated by two bidentate chelating WS₄ tetrahedra, forming a linear $(S_2WS_2ZnS_2WS_2)^{2-}$ unit of three edge-sharing tetrahedra. Bond lengths in the planar four-membered chelate rings are Zn–S = 2.392 (5) Å and W–S = 2.233 (5) Å, while the terminal W–S bonds are 2.156 (6) Å. The nonbonded Zn⋯W distance across the ring is 2.927 (1) Å, the S–Zn–S bond angle in the ring being 96.7 (3)°. The vibrational spectra of the $[Zn(WS_4)_2]^{2-}$ complex were measured and interpreted, using data from samples with pure ⁶⁴Zn and ⁶⁸Zn isotopes.

Introduction

Novel transition-metal complexes containing simple transition-metal complexes as ligands have been prepared as thio- or selenometalatometalates (e.g., $[Ni(WS_4)_2]^{2-}$) by our group for the first time.[2] The vibrational spectra gave evidence that the anions act as bidentate ligands.[3] Electronic, ESR, and magnetic measurements demonstrated the existence of strong metal–ligand interactions.[4] This demonstrates that there is an interesting type of bonding in the bridge system $S_2MS_2M'S_2MS_2$ (M = Mo, W; M' = transition metal of the first row) with a strongly delocalized π-electron system.

Since no structural data such as bond distances are known for this class of compounds, we have determined the crystal structure of $[P(C_6H_5)_4]_2[Zn(WS_4)_2]$, single crystals of which could be obtained. We have also measured the vibrational spectra of the compound with ⁶⁴Zn and ⁶⁸Zn isotopes to obtain additional information about the type of complexation and an understanding of the coupling between the stretching vibrations (see also ref 5).

Experimental Section

Preparation. Tetraphenylphosphonium bis(tetrathiotungstato)-zincate(II), $[P(C_6H_5)_4]_2[Zn(WS_4)_2]$, was prepared by adding an aqueous solution of tetraphenylphosphonium chloride to an aqueous solution of ZnCl₂ containing (NH₄)₂WS₄ in excess (see also ref 6). The compounds with Zn isotopes were prepared on a milligram scale. ⁶⁴Zn (99.66%) and ⁶⁸Zn (98.5%) were purchased from Oak Ridge National Laboratory. The crystals used for the structure determination were obtained as yellow elongated prisms (prism axis c) by mixing the solution of the compound in dimethylformamide with 96% ethanol.

Measurement of the Spectra. The infrared spectra were measured on a Perkin-Elmer Model 180 (4000–140 cm⁻¹). The Nujol mull technique with CsI (4000–200 cm⁻¹) or polyethylene plates (400–140 cm⁻¹) was employed. The frequency reading was checked by running the spectra of standard compounds for calibration.[7,8] The Raman spectra of the solid compounds mixed with KBr (ratio 1:1) were obtained with a Coderg PHO instrument equipped with a krypton laser, using the 15 453.5-cm⁻¹ line.

Collection and Reduction of the X-Ray Data. Weissenberg and precession photographs showed that the crystals belong to the tetragonal system, the observed systematic absences $h + k + l = 2n + 1$ for hkl and the Laue symmetry $4/m$ being consistent with the space groups $I4$, $I\bar{4}$, and $I4/m$.

The unit cell parameters obtained at 22 °C by least-squares refinement of the diffractometer angular coordinates of 13 high-angle reflections are $a = b = 13.292$ (5) Å, $c = 6.890$ (2) Å. The experimental density, $d_{exptl} = 1.88$ (2) g/cm³, determined pycnometrically under benzene, is in good agreement with the calculated value, $d_{calcd} = 1.866$ g/cm³, for $Z = 1$ formula unit.

Closer inspection of overexposed photographs showed a system of much weaker, diffuse reflections which indicated a unit cell larger by a factor of 4, being body-centered tetragonal like the smaller one and being related to it by $a' = a + b = 18.800$ (7) Å, $c' = 2c = 13.780$ (4) Å. Because a precise evaluation of the diffuse intensities was doubtful, it was decided at this point to start with a determination of the substructure and to try to explain the superstructure in a second step.

X-ray intensity data for a 0.08 × 0.08 × 0.12 mm single crystal were collected at 22 °C on a Syntex $P2_1$ computer-controlled four-circle diffractometer, using graphite-monochromated Mo Kα radiation (λ (Kα) 0.70926 Å, $\lambda(K\alpha_2)$ 0.71354 Å, ω–2θ scan, scintillation counter, takeoff angle 4°). The sampling interval (in 2θ) for each reflection was from 1.0° below the calculated Mo Kα₁ maximum to 1.0° above the calculated Mo Kα₂ maximum. The scan rate varied from 1.2°/min to 15°/min (in 2θ), depending on the intensity of the reflection. Background measurements were made at the beginning and the end of each scan with the counter stationary; the total time for background counts was equal to the scan time. The intensity of a standard reflection measured at 50 reflection intervals showed no significant change during data collection.

A total of 720 unique reflections were obtained by averaging the data of two octants (hkl and $hk\bar{l}$) measured in the range of $(\sin\theta)/\lambda$ between 0.03 and 0.64 Å⁻¹. No significant intensities were observed for the reflections classified above as systematically absent; no deviation from tetragonal symmetry was noticed. The linear absorption coefficient for Mo Kα radiation is $\mu = 59.2$ cm⁻¹ giving μr values (r radius) between 0.32 and 0.39 for the crystal used. No absorption and anomalous dispersion corrections were applied to the Lp corrected data. Standard deviations for the net intensities were determined according to the counting statistics.

Determination and Refinement of the Substructure. The acentric space groups $I\bar{4}$ and $I4$ were favored by intensity statistics. From these $I\bar{4}$ was chosen, because the $\bar{4}$ axes were expected to be possible sites for at least some of the tetrahedrally coordinated central atoms (Zn, W, P).

Since the number of equivalent positions in the space group $I\bar{4}$ is at least 2 and since there is only one $[Zn(WS_4)_2]^{2-}$ ion per unit cell, some kind of disorder of the structure was expected from the beginning. The positions of the Zn, W, S, and P atoms including the partial occupation of the Zn, W, and S sites were determined from the three-dimensional Patterson function. The strongest Patterson vector was found on the twofold axis (0, 0, z; $z = 0.147$) with a length of only 1 Å. This vector was interpreted as a W–W distance resulting from partial occupation of the site 4e (0, 0, z etc.) with $z = 0.574$, the positions 0, 0, z or 0, 0 $\bar{z}$ (and, respectively, $^1/_2$, $^1/_2$, z or $^1/_2$, $^1/_2$, $^1/_2 - z$) being alternatively occupied tungsten positions. A probable W–S vector with two parallel satellites differing from the first only by about ±1 Å in z yielded a structure model of two WS₄ tetrahedra alternatively fitting with one of the statistically occupied W sites. The Zn and P positions were determined from the Patterson map to be

Table I. Fractional Atomic Coordinates and Thermal Parameters,^{a} Referring to the Cell with $a = 13.292$, $c = 6.890$ A, with Standard Deviations

Atom	No. of equiv posn	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Zn	2^b	0.0	0.0	0.0	4.02 (20)	4.02 (20)	1.93 (12)	0	0	0
W	4^b	0.0	0.0	0.5752 (1)	2.68 (9)	1.85 (7)	1.95 (3)	−0.18 (7)	0	0
S(1)	8^b	0.0392 (4)	0.1287 (4)	0.7693 (8)	4.20 (24)	2.19 (18)	2.73 (19)	−1.01 (17)	0.04 (19)	−0.30 (17)
S(2)	8^b	−0.1265 (4)	0.0378 (5)	0.3933 (8)	3.51 (24)	3.95 (25)	3.05 (23)	−0.92 (20)	0.89 (21)	0.37 (22)
P	2	0.0	0.5	0.75	2.43 (21)	2.43 (21)	2.81 (20)	0	0	0
C(1)	8	0.0471 (7)	0.4017 (7)	0.9073 (16)	3.23 (37)	2.46 (34)	3.60 (37)	0.20 (29)	−0.30 (44)	0.96 (41)
C(2)	8	0.1490 (7)	0.3745 (9)	0.9023 (17)	2.69 (37)	5.06 (53)	3.68 (42)	−0.25 (35)	−1.30 (45)	−1.02 (48)
C(3)	8	0.1795 (8)	0.2966 (9)	0.0294 (17)	4.29 (44)	5.61 (51)	3.38 (65)	1.86 (39)	0.03 (44)	0.07 (45)
C(4)	8	0.1136 (12)	0.2501 (12)	0.1468 (17)	5.40 (68)	5.91 (76)	3.97 (51)	1.22 (58)	0.45 (47)	1.43 (46)
C(5)	8	0.0109 (12)	0.2781 (12)	0.1514 (16)	5.89 (73)	6.00 (76)	3.46 (49)	1.76 (61)	0.56 (45)	1.72 (46)
C(6)	8	−0.0222 (8)	0.3557 (8)	0.0310 (16)	4.44 (44)	4.51 (43)	2.80 (61)	1.55 (36)	0.67 (38)	0.76 (38)

^{a} The anisotropic temperature factor is used as $\exp[-{}^1/_4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$. ^{b} Occupancy factor of 0.5 for Zn, W, S(1), and S(2) due to statistical disorder.
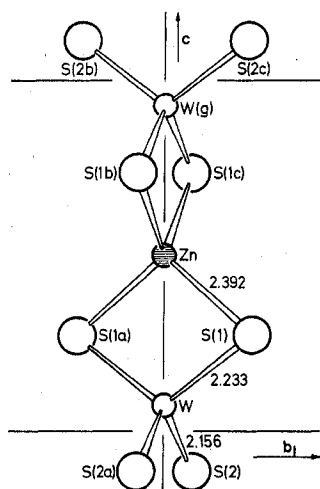

Figure 1. $[Zn(WS_4)_2]^{2-}$ ion with atomic designations and bond lengths in Å.

2a (0, 0, 0) and 2d (0, $^1/_2$, $^3/_4$). Since chemical analysis and experimental density only allow one Zn per unit cell, the population factor was reduced to half its full value, as has been done for the W and S atoms.

The starting parameters (with individual isotropic temperature factors) were refined to $R = 0.168$. The phenyl carbon atoms were successfully located from the subsequent ΔF map phased by the W, Zn, S, and P atoms. Full-matrix least-squares refinement of the scale factor and the positional and isotropic thermal parameters of all nonhydrogen atoms converged to residuals of $R_1 = 0.058$ and $R_2 = 0.060$ for all 720 reflections, where $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$. The quantity minimized was $\sum w(|F_o| - |F_c|)^2$. The weighting scheme was based on the standard deviations of the scan counts with an additional term proportional to the net intensity: $w = 4F_o^2/(\sigma(F_o^2))^2$ with $\sigma(F_o^2) = [(\sigma(I))^2 + (0.03I)^2]^{1/2}Lp^{-1}$. Reflections with $I < 2\sigma(I)$ were classified as unobserved and given zero weight (83 reflections). The atomic scattering factors for W, Zn, S, P, and C were taken from ref 9. After several cycles of refinement with anisotropic thermal parameters, the shifts of all variables in the last cycle were below 0.05σ. The following final residuals were obtained: $R_1 = 0.044$, $R_2 = 0.043$ (for all reflections) and $R_1 = 0.038$, $R_2 = 0.043$ (only observed reflections), the final standard deviation of an observation of unit weight being 1.68 e. In all final refinements the occupancy factors of Zn, W, S(1), and S(2) were taken constant as 0.5 according to the statistical structure model. Their inclusion as variables into the refinement gave no significant change of the starting values. The final difference Fourier map contained no significant peaks except near the tungsten sites (up to 3 e/Å^3) which were attributed to series termination effects. Especially at or near the statistically nonoccupied Zn sites, there was no clear indication of possible additional atoms (see discussion below).[10]

The final positional and thermal parameters are given in Table I. A list of observed and calculated structure factor amplitudes (also

Table II. Interatomic Distances (A) and Bond Angles (deg) in the $[Zn(WS_4)_2]^{2-}$ and $[P(C_6H_5)_4]^+$ Ions^a

$[Zn(WS_4)_2]^{2-}$ Bonded Distances

W–S(1)	} 2.233 (5)	Zn–S(1)	
W–S(1a)		Zn–S(1a)	} 2.392 (5)
W–S(2)	} 2.156 (6)	Zn–S(1b)	
W–S(2a)		Zn–S(1c)	

$[Zn(WS_4)_2]^{2-}$ Bond Angles and Nonbonded Distances^b

	Bond Angle	S···S distance
S(1)–W–S(1a)	106.4 (3)	3.575 (9)
S(1)–W–S(2) S(1a)–W–S(2a)	} 110.6 (2)	3.608 (8)
S(1)–W–S(2a) S(1a)–W–S(2)	} 110.2 (2)	3.599 (8)
S(2)–W–S(2a)	108.9 (3)	3.509 (10)
S(1)–Zn–S(1a) S(1b)–Zn–S(1c)	} 96.7 (3)	3.575 (9)
S(1)–Zn–S(1b) S(1)–Zn–S(1c) S(1a)–Zn–S(1b) S(1a)–Zn–S(1c)	} 116.2 (3)	4.062 (10)
W–S–Zn	78.5 (2)	

$[P(C_6H_5)_4]^+$ Bond Distances

P–C(1)		C(1)–C(2)	1.403 (14)
P–C(1d)	} 1.810 (10)	C(1)–C(6)	1.395 (15)
P–C(1e)		C(2)–C(3)	1.415 (17)
P–C(1f)		C(3)–C(4)	1.343 (18)
		C(4)–C(5)	1.414 (22)
		C(5)–C(6)	1.396 (18)

$[P(C_6H_5)_4]^+$ Bond Angles

C(1)–P–C(1d)	} 106.4 (5)	C(2)–C(1)–C(6)	122.7 (9)
C(1e)–P–C(1f)		C(1)–C(2)–C(3)	116.7 (10)
C(1)–P–C(1e)		C(2)–C(3)–C(4)	121.5 (11)
C(1)–P–C(1f)	} 111.0 (5)	C(3)–C(4)–C(5)	121.4 (12)
C(1d)–P–C(1e)		C(4)–C(5)–C(6)	119.1 (12)
C(1d)–P–C(1f)		C(5)–C(6)–C(1)	118.6 (10)

^{a} The indices refer to the following transformations of the atomic coordinates given in Table I: (a) $\bar{x}, \bar{y}, z$; (b) $y, \bar{x}, 1 - z$; (c) $\bar{y}, x, 1 - z$; (d) $x, 1 - y, z$; (e) $^1/_2 - y, ^1/_2 + x, ^1/_2 - z$; (f) $-^1/_2 + y, ^1/_2 - x, ^1/_2 - z$; (g) $\bar{y}, x, \bar{z}$. ^{b} W···Zn = 2.927 (1) A.

of the superstructure reflections, see below) is available.[11]

Description and Discussion of the Structure

The crystal structure consists of discrete $[Zn(WS_4)_2]^{2-}$ and $[P(C_6H_5)_4]^+$ ions. Figure 1 shows the anion with atomic designations and bond lengths. The anion forms a novel type of mononuclear complex and consists of a central ZnS$_4$ tetrahedron sharing edges with two WS$_4$ tetrahedra. Thus, the WS$_4^{2-}$ ions act as bidentate chelating ligands toward Zn^{2+}, as has been predicted from the vibrational spectra.[6]

In Table II bond lengths, bond angles, nonbonded distances between neighboring S atoms, and the Zn···W distances within the $[Zn(WS_4)_2]^{2-}$ ion as well as bond lengths and angles in the cation are listed together with their standard deviations. According to the exact crystallographic $\bar{4}$ site symmetry of the complex anion, the four-membered ZnS_2W chelate rings are constrained to being exactly planar, the four Zn–S bonds being equal in length (2.392 (5) Å) and the W–S bridging and terminal bonds being equal in pairs of two.

As expected, the terminal bonds (2.156 (6) Å) in the slightly distorted WS_4 tetrahedra are shorter than the chelating ones (2.233 (5) Å). Comparison with the mean W–S bond lengths in the isolated WS_4^{2-} (2.17 (1) Å in the ammonium salt[12]), WOS_3^{2-} (2.198 Å with individual values 2.193 (6)–2.206 (6) Å in $K_3WOS_3Cl^{13}$), and $WO_2S_2^{2-}$ (2.193 (2) Å in the ammonium salt[14]) ions show that the chelating W–S bridge bonds in the complex are slightly longer, as is to be expected. The average value over all four bonds in the complex WS_4 group (2.195 Å), however, is in very good agreement with the data for the free ions.

The tetrahedral environment of Zn^{2+} is strongly disorted with S–Zn–S bond angles of 96.7 (3)° within the strained four-membered ZnS_2W rings. This distortion, being mainly caused by repulsion between the central atoms of the tetrahedra, is observed in a very similar form in the four-membered ZnS_2P and ZnS_2C chelate rings of dithiophosphinato,[15] dithiophosphato,[16,17] dithiobenzoato,[18] xanthato,[19] or dithiocarbamato[20,21] zinc complexes. Another consequence of the strain in the four-membered rings is a significant lengthening of the Zn–S bonds compared to unstrained systems. The bond length of 2.392 (5) Å in $[Zn-(WS_4)_2]^{2-}$ compares with mean values in the range of 2.37–2.41 Å (individual distances ranging from 2.307(4)–2.509(8) Å) in the four-membered rings formed with the bidentate ligands above,[15-21] whereas the normal Zn–S bond lengths in unstrained complex systems (chains, larger rings, unidentate ligand complexes; see also ref 15–21 and literature cited therein) are observed at values between ca. 2.28 and 2.35 Å.

The symmetric structure of the four-membered chelate ring in $[Zn(WS_4)_2]^{2-}$ is in contrast to the given examples of ZnS_2P and ZnS_2C chelate rings where there is invariably one short and one longer Zn–S bond differing significantly by about 0.03–0.10 Å.[15-21]

Bond lengths and angles in the $[P(C_6H_5)_4]^+$ ion with exact $\bar{4}$ symmetry are, within the limits of error, in close agreement with literature data. The P–C distance of 1.810 (10) Å, which is slightly longer than other reported values, and the average C–C bond length of 1.39 (2) Å in the phenyl rings compare with mean values such as 1.796 (3) and 1.390 (11) Å,[22] 1.775 (7) and 1.391 (11) Å,[23] or 1.790 (8) and 1.40 (2) Å[24] for tetraphenylphosphonium ions in different compounds. There is no significant deviation from planarity observed in the phenyl rings.

The crystal structure can be described as an arrangement of stacks parallel to the c axis (a) of cations at $x = 0$, $y = 1/2$, and $x = 1/2$, $y = 0$ with identity periods of $c = 6.890$ (2) Å and (b) of anions at $x = 0$, $y = 0$ and $x = 1/2$, $y = 1/2$ with periods $2c = 13.780$ (4) Å. *Within* the individual stacks, the anions are constrained to an essentially *ordered* occupation of every second unit cell. As there are two such anion sites possible in every stack, the unit cell with $c = 6.890$ Å describes a statistical average structure, being an arbitrary arrangement of individual stacks in relation to each other with independent filling of one of the two possible anion sites.

In this sense, Figure 2 shows only one possible realization of this statistical anion distribution. The disorder is favored by the fact that the space-determining sulfur atoms have to
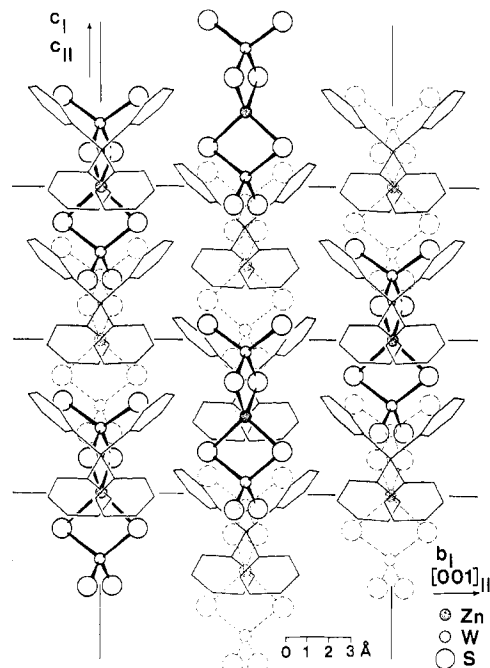

Figure 2. Projection of the $[P(C_6H_5)_4]_2[Zn(WS_4)_2]$ structure parallel to the *a* axis of the substructure cell I. One of the several possible relative orientations of the $[Zn(WS_4)_2]^{2-}$ anion stacks is given in solid lines with the alternative positions of the anions represented in dotted lines; the partial ordering of the anions (*I* centering of the superstructure cell II) is indicated.

be shifted only about 1.0 Å parallel to c to change from one anion stack to the alternate one, inferring minimal disturbance to the rest of the structure. All intermolecular contacts are normal for the alternate arrangements except around the site of the nonoccupied Zn position (shortest S···S distance between two neighboring anions within one stack: 5.96 Å; see discussion below).

The Superstructure. The additional diffuse reflections indicate that the distribution of the anion stacks is *not* strictly random. Using modified measuring parameters (sampling interval 6° instead of 2° in 2θ, counter aperture diameter 5 mm instead of 2.5 mm, scan rate 0.5°/min), the approximate integrated intensities of 1339 (1009 classified as observed) supercell reflections with $l' \neq 2n$ were measured. They could be indexed on the basis of a body-centered cell (cell II) with $a' = a + b$, $c' = 2c$, with no extinctions except $h' + k' + l' \neq 2n$. As to be expected, no additional significant reflections besides the substructure ones were registered in the layers with $l' = 2n$.

A solution of the superstructure problem could be reached assigning the space group $I\bar{4}$ also for cell II. This space group for the larger cell results from a two-step supergroup–maximal subgroup symmetry-reduction procedure[25] in the following way: removal of $\bar{4}$ at $1/4$, 0, $1/4$ etc. in the substructure cell I leads to $P\bar{4}$ as the maximal subgroup which is further reduced to maximal subgroup $F\bar{4}$ by doubling a, b, and c and removal of $\bar{4}$ at 0, 0, $1/4$ etc. and $1/4$, $1/4$, 0 etc. of this new cell. $F\bar{4}$ is identical with $I\bar{4}$ in the diagonal setting of cell II ($V_{II} = 4V_I$).

Using only the reflections of the odd (diffuse) layers of cell II ($l \neq 2n$), a good fit between observed and calculated structure amplitudes was obtained by placing nothing but one $[Zn(WS_4)_2]^{2-}$ anion at 0, 0, 0 etc., refining the transformed coordinates and the isotropic temperature factors of the subcell. The final R_1 value for this model was 0.107 with isotropic temperature factors for W, Zn, and S, which was accepted as satisfactory in view of the difficulties in obtaining reasonably precise intensities for the diffuse reflections. The atomic

Table III. Vibrational Spectra of $[^{64}Zn(WS_4)_2]^{2-}$ and $[^{68}Zn(WS_4)_2]^{2-}$ in the Tetraphenylphosphonium Salts above 200 cm^{-1}

Freq data, cm^{-1}			Assign^e	
IR^a	R	$\Delta\nu^c$	D_{2d}	Vib
d	494 (10)		A$_1$	$\nu_s(WS_2{}^t)$ ip
492.4 sh			B$_2$	$\nu_s(WS_2{}^t)$ op
487.2 s			E	$\nu_{as}(WS_2{}^t)$
d	447 (2)		A$_1$	$\nu_s(WS_2{}^b)$ ip
435 sh			B$_2$	$\nu_s(WS_2{}^b)$ op
445.5 s		0.7	E	$\nu_{as}(WS^b)$
d	b		A$_1$	$\nu_s(ZnS)$
285 sh		5	B$_2$	$\nu_{as}(ZnS)$
271.5 w		1.5	E	$\nu_{as}(ZnS)$

^{a} Data of $[^{68}Zn(WS_4)_2]^{2-}$. ^{b} Overlapped by bands of the cation. ^{c} $\Delta\nu = \nu[^{64}Zn(WS_4)_2]^{2-} - \nu[^{68}Zn(WS_4)_2]^{2-}$. ^{d} Inactive. ^{e} Assignment of $\nu(WS_2)$ to in-phase (ip) and out-of-phase (op) vibrations.

coordinates did not change by more than 1.5σ from the substructure values. The refined scale factor (3.26 (2) vs. 1.564 (2) for the statistical even-layer substructure model) indicates only partial (ca. 50%) superstructure ordering.

Summarizing, the partially ordered structure model can be described as follows: The neighboring anion stacks parallel to c are not completely independent from each other with respect to the occupation of the two possible anion sites of the statistical model. Referring to the larger superstructure cell II, an I centering relation between the different anion stacks is partially retained. No modification of the cation part of the structure is necessary: the $(C_6H_5)_4P^+$ ions which are at $\bar{4}$ sites at 0, $^1/_2$, $^3/_4$ etc. in cell I remain at their locations, now on 2_1 axes at $^1/_4$, $^1/_4$, $^1/_8$ etc. in cell II. The diffuse character of the superstructure reflections (half-widths of the approximately spherical reflections 0.6–1.2° in θ) on weak background of diffuse scattering especially along the rl planes with $l' \neq 2n$ is indicative of the limited degree of order within the superstructure symmetry. The most probable cause is rotational anion disorder around the c direction together with librational displacements in the ab plane. In any case, the average substructure gives a very close picture of the true anion and cation dimensions; part of the disorder effects are evidently absorbed in the temperature factor coefficients of the average structure.

A question which remains open is the possible occupation of the site at or around 0, 0, $^1/_2$ etc. by ordered or disordered water molecules. For the structure model described this site is surrounded by four S(2) atoms at a distance of 3.228 (6) Å and eight phenyl hydrogen atoms (bonded to C(4) and C(5), calculated coordinates), at ca. 3.55–3.66 Å distance, this void being large enough to keep one H$_2$O molecule. From ΔF Fourier syntheses in both superstructure and substructure cells, however, no significant electron density of more than 1 e/Å^3 and no refinable atomic positions were found. Yet, partial highly disordered H$_2$O occupation of this site cannot be excluded completely. One H$_2$O per anion would result in d_{calcd} = 1.891 g/cm^3.

Vibrational Spectra. The measured infrared and Raman frequencies of $[Zn(WS_4)_2]^{2-}$ with ^{64}Zn and ^{68}Zn isotopes are summarized in Table III. The approximation of the anion toward an idealized D_{2d} ($\bar{4}2m$) symmetry is very close, so the normal modes of vibration can be classified according to the species of this point group as

$$\Gamma_{vib} = 5 \text{ A}_1 \text{ (R)} + \text{A}_2 (\ldots) + 2 \text{ B}_1 \text{ (R)} + 5 \text{ B}_2 \text{ (R, IR)} + 7 \text{ E (R, IR)}$$

and the stretching vibrations of the two terminal WS$_2{}^t$ groups and the two bridging WS$_2{}^b$ groups and the ZnS$_4$ skeletal vibrations can be classified as

$$\Gamma_{vib} = 3 \text{ A}_1 + 3 \text{ B}_2 + 3 \text{ E}$$

Compared to the stretching frequencies of the WS$_4{}^{2-}$ ion ($\nu_1(A_1) = \nu_s = 479$ cm^{-1}, $\nu_3(F_2) = \nu_{as} = 455$ cm^{-1}),[3] complex bands at higher and lower wavenumbers are observed in the spectrum of the complex. According to the stronger bonding (shorter bond distance) in the terminal W–S bonds, the WS$_2{}^t$ stretching frequencies should be at higher energy.

Corresponding in-phase (ip) and out-of-phase (op) vibrations are similar in frequencies as expected. As the compound is a poor Raman scattering material, only the totally symmetric vibrations are observed in the Raman spectra. It is interesting to note that the intensity of the band due to $\nu(WS_2{}^t)$ is stronger than that of $\nu(WS_2{}^b)$ because of the higher bond order in the terminal group.

Additional information for an understanding of the vibrational spectrum is given from the measured isotopic shifts. The comparison with similar complexes shows that the frequency shifts of the $\nu(ZnS)$ vibrations are in the expected order.[26] The frequencies $\nu(WS_2{}^b)$ show a small shift whereas the frequencies of $\nu(WS_2{}^t)$ are not shifted during ^{64}Zn–^{68}Zn substitution. This nicely demonstrates that there exists only small coupling between the $\nu(ZnS)$ skeletal and the $\nu(WS^b)$ vibrations. The $\nu(WS^t)$ vibrations should be nearly pure normal modes.

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