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Preparation and X-Ray Study of Mixed-Anion Tungsten Dichalcogenides

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Received January 28, 1976 AIC600776

Mixed-anion systems of the tungsten dichalcogenides have been prepared by direct synthesis from the elements. X-ray investigations have been carried out as a function of composition. In the $WS_{2-x}Se_x$ system, there is a continuous series of solid solutions, all having the 2H structure (space group $P6_3/mmc$). The unit-cell parameters increase monotonically as x increases but there is a maximum in the c/a ratio at $x = 1.3$. In the $WSe_{2-x}Te_x$ system, monophasic regions occur for $0 < x < 0.62$, where the structure is 2H, and $1.48 < x \leq 2.00$, where the structure is that of WTe_2 (space group $Pnm2_1$). In the $WS_{2-x}Te_x$ system, corresponding monophasic regions occur for $0 < x < 0.3$ and $1.8 < x \leq 2.0$.

Introduction

The layered dichalcogenides hold great promise as model compounds for study of phenomena in quasi-two-dimensional systems.[1] The 4B and 6B compounds, which are typically semiconductors in the pure stoichiometric state, have added interest as antifriction agents, catalysts, and catalyst supports for hydrodesulfurization reactions,[2] precursors of intercalation superconductors,[3] and current-controlled negative-resistance switches.[4] Recent studies have concentrated on electronic band structures of these materials,[5] but there remain unresolved questions relating to crystallographic structure and the influences that govern formation of specific polytypes under different conditions. Partial cation substitution has proved to be a useful tool for manipulation of conduction electron density, but there has been relatively little effort to exploit anion replacement as a way to fine-tune structural constants. As part of a larger effort to understand cooperative phenomena in quasi-two-dimensional systems, this investigation was undertaken to fix the x-ray structural relations in the mixed-anion compounds of tungsten. The compounds $WX_{2-x}X'_x$ (X, X′ = S, Se, Te) are relatively little known and the evolution of their structural parameters should prove useful in understanding the properties of layered compounds.

The systems investigated in this work are $WS_{2-x}Se_x$, $WSe_{2-x}Te_x$, and $WS_{2-x}Te_x$. The case of $WS_{2-x}Se_x$ is particularly simple in that both end members WS_2 and WSe_2 have the same hexagonal 2H-MoS_2 structure (*C*7 in the Strukturbericht classification). In the structure, the metal atoms are in trigonal-prismatic coordination between two superimposable sheets of hexagonally packed chalcogen atoms, and the M atoms of a sandwich X–M–X lie over the X atoms of the adjacent sandwich. The stacking sequence is AbA BaB; the space group, $P6_3/mmc$. Systems containing tellurium are expected to be more complicated than this, since the tellurium atom is considerably larger than selenium or sulfur and the WTe_2 structure is quite different.[6] The space group of WTe_2 is $Pnm2_1$ (orthorhombic) and there is distorted octahedral coordination about the tungsten atoms. The off-center position of the tungsten atom buckles the tellurium layers and allows tungsten atoms in adjacent octahedra to approach each other. The structure is more like that of CdI_2 (*C*6 type) than of MoS_2 (*C*7 type).

Experimental Section

Preparation of Samples. Starting materials were as follows: tungsten powder, 99.95% (Atomergic); sulfur lumps, 99.9999% (Atomergic); selenium shot, 99.99% (Ventron-Alfa); tellurium lumps, 99.999% (Ventron-Alfa). The elements were weighed in desired stoichiometric amounts and sealed in a quartz tube after evacuation through a liquid nitrogen trap to 10^{-4} Torr for 4 h. In order to minimize thermal gradients, the quartz tube was wrapped in a Kanthal wire coil. The first heating was to 600 °C in steps of 50 °C with two plateaus of 2 h each at 200 and 400 °C. After being kept overnight at 600 °C, the tubes were progressively raised to 900 °C, where reaction was allowed to proceed for 3 days. The next stages were cooling to ambient temperature, shaking of the powder samples until they flowed freely, and reheating at 850 °C for 1 day. This procedure was repeated twice. At the end of the third heating, the samples were cooked for an additional 2 days. The overall procedure took 7 days. After 4 days, the x-ray patterns showed broad lines indicative of stacking disorder; after 7 days, the lines were narrow and no further improvement took place on further heating.

Table I. Unit-Cell Parameters for $WS_{2-x}Se_x$

x	a,[a] Å	c,[b] Å	c/a
0.000	3.161	12.358	3.910
0.182	3.169	12.443	3.926
0.604	3.195	12.625	3.951
0.808	3.207	12.698	3.959
1.014	3.218	12.748	3.961
1.251	3.234	12.830	3.967
1.508	3.251	12.890	3.965
1.603	3.260	12.914	3.961
1.754	3.272	12.956	3.960
2.000	3.286	12.983	3.951

[a] ±0.002 Å. [b] ±0.005 Å.

The samples were not analyzed after reaction, since unreacted chalcogen would easily have been detected by coloring on the tubes and by characteristic garlic-like odor when the tubes were opened. Unreacted tungsten would have been detected by x-rays to as little as 0.3% by weight.

X-Ray Investigation. Both powders and single crystals were studied, but the main structural determinations were done on powders. The powder camera was of the Debye–Scherrer type and had a diameter of 114.6 mm. Radiation was nickel-filtered copper Kα. Specimens were contained in 0.2-mm glass capillaries. Tungsten was used as internal standard for correction of absorption shift. Exposure times ranged from 12 h for specimens containing up to 30 mol % tellurium to as much as 40 h in the case of WTe_2.

All lines on the diffraction patterns were read to 0.05 mm. After correction for absorption and film shrinkage, unit-cell parameters were calculated with a least-squares computer program for both the forward-reflection ($0 < \theta < 45°$) and back-reflection ($45 < \theta < 90°$) regions. Parameters for the two domains were identical within an error range of 0.0005–0.001 Å. Because we wished to have a consistent set of results and because the back-reflection lines for WTe_2 and related structures were difficult to read, all of the unit-cell parameters reported below were based on the forward-reflection lines.

Results

$WS_{2-x}Se_x$ Solid Solutions. Table I presents the results obtained for the sulfur–selenium system. The dependence of a, c, and c/a on x can be represented as

$$a\ (\text{Å}) = 0.00555x^2 + 0.05272x + 3.1601$$

$$c\ (\text{Å}) = -0.0823x^2 + 0.4786x + 12.359$$

$$c/a = -0.0327x^2 + 0.0849x + 3.9111$$

The standard deviation on a ranged from ±0.005 Å for WS_2 to ±0.0008 Å for WSe_2, and on c, from ±0.013 Å for WS_2 to ±0.002 Å for WSe_2. For comparison with other work, it may be noted that Wildervanck and Jellinek[7] have reported

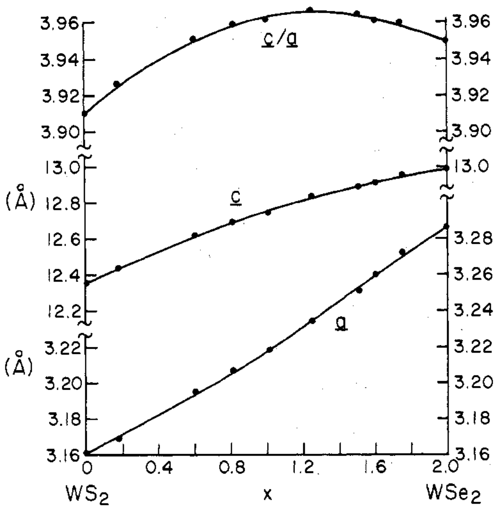

Figure 1. Variation of unit-cell parameters *a*, *c*, and *c*/*a* with composition in the system $WS_{2-x}Se_x$.

for the 2H polytype of WS_2 $a = 3.155$ Å and $c = 12.35$ Å. For 2H-WSe_2, previously reported *a* values are 3.285 ± 0.001,[8] 3.282 ± 0.004,[9] 3.286,[10] 3.285,[11] and 3.2860 ± 0.0002 Å.[12] Respective *c* values are 12.96 ± 0.01, 12.937 ± 0.01, 12.976, 12.984, and 12.978 ± 0.001 Å. It should be noted, as represented in Figure 1, that in the mixed sulfur–selenium system, although *a* and *c* show monotonic rises from WS_2 to WSe_2, the value of *c*/*a* peaks at $WS_{0.7}Se_{1.3}$. Such behavior is most unusual.

Although Sproul and Richman[13] reported the possibility of W_3Se_4 occlusions in WSe_2 crystals, attempts in this research to produce nonstoichiometric WSe_{2-x} (e.g., by heating a 3:4 mixture of W and Se at 1200 °C for a period of 1 month) gave only WSe_2 and W. This lack of deviation from stoichiometry agrees with a similar conclusion by Hicks,[12] who found no significant change in *a* or *c* parameters in the range $WSe_{1.98-2.02}$.

In an attempt to prepare lead-intercalated mixed-anion systems, the compounds $WS_{0.749}Se_{1.251}$, $WS_{1.192}Se_{0.808}$, and $WS_{0.397}Se_{1.603}$ were heated with lead. It was found that the Pb quantitatively pulls out Se to form PbSe and a mixed-anion tungsten compound of higher S:Se ratio.

$WSe_{2-x}Te_x$ System. Table II presents the results obtained for the selenium–tellurium system. The most striking point is that, although the system is monophasic in the selenium-rich region (designated as α) and in the tellurium-rich region (designated as β), two phases are found in the intermediate range $\sim 0.62 < x < \sim 1.48$. The structure in the α region is that of WSe_2 (hexagonal 2H) and in the β region is that of WTe_2 (orthorhombic). In the intermediate range, the two phases found are an α phase, which has the same 2H structure as WSe_2, and a new phase (labeled 2β in Table II) which differs in structure from WTe_2 but is related to it. Basically, the 2β and β (i.e., WTe_2) patterns are almost similar, but for 2β there are many faint lines between the lines corresponding to the β structure. The extra lines can be explained by assuming a superstructure for which the parameters are simply twice those of the β structure, hence the designation 2β.

To facilitate comparison between the α and β regions, a *b* parameter can be derived for the 2H structures as equal to $3^{1/2}a$. As shown in column 4 of Table II, values of *b* so derived rise monotonically with *x* from $x = 0$ to $x = 0.610$, then level off in the range $0.610 < x < 1.484$, make a sharp jump at $x = 1.689$, and finally fall to the value characteristic of pure WTe_2. The orthorhombic WTe_2 structure, which was reported by Brown[6] to have $a = 6.282$, $b = 3.496$, and $c = 14.073$ Å can be regarded as a superstructure of an idealized 2H structure, its relation to 2H being given by $a(WTe_2) = a_0(2H)$, $b(WTe_2) = 3^{1/2}a_0(2H)$, and $c(WTe_2) = c_0(2H)$. (Actually, as mentioned above, the W in WTe_2 is in distorted octahedral sites, not trigonal prismatic, so that WTe_2 might be visualized as a distorted 2T structure with $a:3^{1/2}a:c$ superstructure.)

Table II. Unit-Cell Parameters for $WSe_{2-x}Te_x$

x	Phase	*a*, Å	*b*,[a] Å	*c*, Å	*c*/*a*
0.000	α	3.286	5.692	12.983	3.951
0.045	α	3.294	5.705	13.046	3.961
0.124	α	3.302	5.719	13.099	3.967
0.187	α	3.308	5.730	13.139	3.972
0.248	α	3.312	5.737	13.187	3.982
0.358	α	3.323	5.756	13.284	3.998
0.610	α	3.346	5.795	13.451	4.020
0.752	α	3.344	5.792	13.438	4.019
	2β	6.872	12.597	27.817	4.048
0.898	α	3.347	5.797	13.449	4.018
	2β	6.886	12.580	27.82	4.040
0.998	α	3.347	5.797	13.460	4.022
	2β	6.87	12.573	27.79	4.045
1.000	α	3.345	5.794	13.429	4.015
	2β	6.89	12.590	27.84	4.041
1.007	α	3.346	5.795	13.436	4.016
	2β	6.882	12.566	27.78	4.037
1.222	α	3.349	5.801	13.449	4.016
	2β	6.887	12.569	27.81	4.038
1.484	α	3.374	5.844	13.433	3.981
	2β	6.89	12.59	27.81	4.036
1.689	β	3.442	6.319	13.929	4.047
1.705	β	3.444	6.308	13.983	4.060
1.810	β	3.470	6.263	14.037	4.045
1.879	β	3.474	6.317	14.027	4.038
1.959	β	3.482	6.299	14.035	4.031
2.000	β	3.483	6.265	14.043	4.032

[a] For the α phase, the *b* parameter is derived as $3^{1/2}a$.

For comparison of the 2β with the 2H structure, the *a*, *b*, and *c* parameters of the 2β structure would correspond respectively to $2a_0$, $2(3^{1/2})a_0$, and $2c_0$ of the 2H structure. Although it is possible that the 2β structure may have a slight monoclinic deformation (as for β-$MoTe_2$[6] and $VS_{1.64}$ or $VS_{1.47}$[14]), there was no experimental evidence in the powder diffraction patterns for such deformation.

The least-squares derived expressions for the lattice parameters of $WSe_{2-x}Te_x$ are as follows: for the α region (2H structure)

$$a\,(\text{Å}) = -0.009207x^2 + 0.099497x + 3.289$$

$$c\,(\text{Å}) = -0.14462x^2 + 0.8376x + 12.995$$

and for the β region (WTe_2 structure)

$$a\,(\text{Å}) = -0.55538x^2 + 2.1801x + 1.3422$$

$$b\,(\text{Å}) = 0.035486x^2 - 0.22432x + 6.5874$$

$$c\,(\text{Å}) = -2.5046x^2 + 9.5041x + 5.0357$$

It should be noted that, since the phase diagram has been established by x-ray diffraction on compounds that have been prepared at 850–900 °C and then cooled slowly after several heatings, the domain boundaries between the α and β single-phase regions and the two-phase region containing α and 2β are not very sharply defined. Alternate procedures, such as quenching of the samples from 850–900 °C, would not give well-defined products since at these temperatures appreciable amounts of the two chalcogenides are in the vapor phase.

From Figure 2, which shows the variation of *a* and of *c* as functions of *x* for all three phases (α, 2β, and β) of $WSe_{2-x}Te_x$, it can be seen that except for the central biphasic region the variation of *a* is linear with *x* and roughly of the same slope for both α- and β-type compounds. On the other hand, the

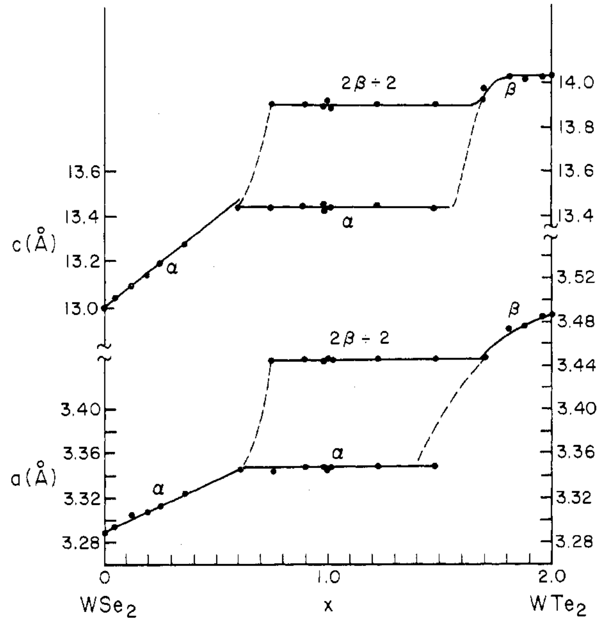

Figure 2. Variation of unit-cell parameters *a* and *c* with composition in the system $WSe_{2-x}Te_x$. For the 2β phase, the observed parameters have been divided by 2 for ease of comparison.

Table III. Unit-Cell Parameters for $WS_{2-x}Te_x$

x	Phase	a, Å	b,[a] Å	c, Å	c/a
0.000	α_I	3.161	5.475	12.358	3.910
0.0184	α_I	3.166	5.484	12.394	3.915
0.120	α_I	3.168	5.487	12.458	3.932
0.154	α_I	3.180	5.508	12.605	3.964
0.337	α_I	3.179	5.506	12.657	3.981
	α_{II}	3.209	5.558	13.037	4.063
0.391	α_I	3.185	5.517	12.722	3.994
	α_{II}	3.208	5.556	13.068	4.074
0.594	α_I	3.193	5.530	12.753	3.994
	α_{II}	3.210	5.560	13.019	4.056
0.805	α_I	3.198	5.539	12.805	4.004
	α_{II}	3.212	5.563	13.021	4.054
	2β	6.90	12.50	28.16	4.08
0.982	α_I	3.221	5.579	12.897	4.004
	α_{II}			13.019	
	2β	6.90	12.50	28.16	4.08
1.162	α_{II}	3.210	5.560	13.010	4.053
	2β	6.90	12.48	28.13	4.08
1.399	α_{II}	3.205	5.551	13.008	4.059
	2β	6.95	12.48	28.13	4.05
1.593	α_{II}	3.220	5.577	13.024	4.045
	2β	6.89	12.49	28.15	4.08
1.785	α_{II}			13.053	
	2β	6.91	12.47	28.11	4.07
1.848	β	3.450	6.276	14.063	4.076
1.904	β	3.465	6.272	14.062	4.058
1.948	β	3.476	6.278	14.071	4.048
2.000	β	3.483	6.265	14.043	4.032

[a] For the α phases, the *b* parameter is derived as $3^{1/2}a$.

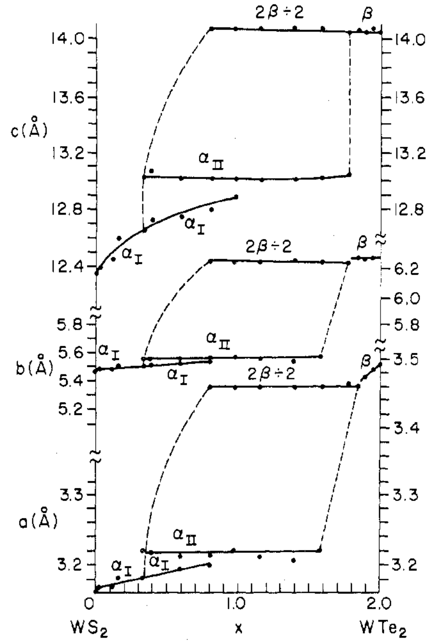

Figure 3. Variation of unit-cell parameters *a*, *b*, and *c* with composition in the system $WS_{2-x}Te_x$. For the α phases, the *b* parameter is taken to be $3^{1/2}a$. For the 2β phase, the points plotted are actually half the observed parameter values.

rate of increase of *c* with *x* for the α phase is much greater than that for the β phase. Thus, we have the interesting situation that, although WSe_2 and WTe_2 phases are of different structure type, their *a* parameter varies in the same manner whereas the *c* parameter varies quite differently. As noted below, this is in line with the fact that structural changes in layered compounds occur mainly in the *c*-axis direction. The fact that the *c* axis expands faster than expected on a pure size basis may be an indication that the tellurium atoms stick out of the chalcogen plane when tellurium is first substituted for sulfur or selenium.

$WS_{2-x}Te_x$ Systems. Table III presents the x-ray parameters observed for the sulfur–tellurium systems. The blanks indicate that the phase, although present, was in too small an amount to characterize properly. Figure 3, which shows the variation of *a*, *b*, and *c* as functions of composition, clearly demonstrates the complexity of the system. Only at the extreme limits, $0 < x < 0.3$ and $1.8 < x < 2.0$, is the system single-phased, hexagonal 2H, and orthorhombic WTe_2, respectively. In the intermediate region, two and even three phases are found. In the range $0.3 < x < 0.8$, there are two α-type phases; in the range $0.8 < x < 1.8$, there are either two of the α type and one of the 2β type or one of the α type and one of the 2β. Phase-rule considerations make it extremely unlikely that the three phases coexist in thermodynamic equilibrium at any temperature. Rather it is more probable that the α_I phase (which has varying unit-cell parameters) crystallizes at different temperatures, whereas the α_{II} and 2β phases (for which unit-cell parameters stay constant despite change in overall composition) may well coexist at some thermodynamic equilibrium temperature. The steady expansion of *a* and *c* with *x* suggests continued dissolution of tellurium in the α_I phase even after the α_{II} phase appears. The fact that the *c* parameter rises much more rapidly than the *a* parameter again, as in the $WSe_{2-x}Te_x$ system, suggests that the first substituted tellurium sits perceptibly out of the chalcogen plane.

At around $x = 0.8$, there appears a 2β phase which, as mentioned above for $WSe_{2-x}Te_x$, can be interpreted in terms of a WTe_2 supercell. Its parameters are constant over the entire existence range $0.8 < x < 1.8$, and there is marked similarity between the unit cell of the 2β phase in the $WS_{2-x}Te_x$ system (e.g., at $x = 1.593$, $a = 6.89$, $b = 12.49$, $c = 28.15$ Å, and $V = 2422$ Å^3) and the unit cell of the 2β phase in the $WSe_{2-x}Te_x$ system (at $x = 1.484$, $a = 6.89$, $b = 12.59$, $c = 27.81$ Å, and $V = 2412$ Å^3). Apparently, the structure is basically decided by the tellurium.

As shown in the upper far right of Figures 2 and 3, when only the β phase is present, there is practically no variation of the unit-cell *c* parameter with *x*. In other words, low-level substitution of either sulfur or selenium for tellurium in the WTe_2 structure makes practically no change in the *c*-direction extension. On the other hand, the *a* axis definitely shrinks on such substitution. We take this as further indication that the *c* parameter is basically decided by tellurium–tellurium repulsions across the van der Waals gap, and these are not affected much by partial replacement of tellurium by the smaller sulfur or selenium atoms. The *a* parameter, however, appears to be fixed mainly by the σ-bonding interactions and directly reflects differences in the covalent radii.

Discussion

The problem of octahedral vs. trigonal-prismatic coordination in the transition metal dichalcogenides has been treated by Gamble[15] in terms of fractional ionic character of the metal–chalcogen bonds. In his plot of cation:anion radius ratio vs. fractional ionic character WS_2 and WSe_2 clearly fall in the trigonal-prismatic region of the diagram whereas WTe_2 is well in the octahedral region. Madhukar[16] suggested a classification based on covalent radii, polarization of the bonding orbitals, and ionicity of the metal–chalcogen bond. WS_2 and WSe_2 again are clearly in the trigonal-prismatic region whereas WTe_2 is just barely in the octahedral region. The apparent equal success of Gamble's and Madhukar's classifications is attributed to coincidental closeness of the ionic and van der Waals radii of the chalcogens and is taken to indicate that size effect is a dominant factor governing trigonal-prismatic vs. octahedral structure.[16]

In the mixed-chalcogen systems of this investigation, size effect seems to be correspondingly important in fixing the expansion of the *a* and *c* parameters except that, in addition, tellurium substitution seems to have a specially large effect on *c*. Pauling's ionicity–electronegativity relation[17] predicts 15, 12, and 4% ionic character for W–S, W–Se, and W–Te bonds, respectively, so a covalent model for tungsten dichalcogenides is indicated. We can make a crude estimate of how the unit-cell parameters should change on substituting one chalcogen for another by using a composition-weighted average radius for the chalcogen in the mixed systems. Assuming ideal prismatic configuration ("ideal" being taken to mean that all edges of the prism are equal) and setting the average chalcogen radius equal to $(x/2)r_1 + (1 - (x/2))r_2$, we can easily show that $\mathrm{d}a/\mathrm{d}x = \cos\theta(r_1 - r_2)$, where a is the unit-cell parameter, x is the composition variable, θ is the prism angle (between the perpendicular to the layer and the tungsten–chalcogen bond direction), and r_1 and r_2 are the radii of the chalcogen atoms in the mixture. For most of the layered dichalcogenides the prism angle turns out to be remarkably close to the ideal value of 49.107°. Using standard covalent radii (S, 1.04 Å; Se, 1.14 Å; Te, 1.32 Å), we can calculate that $\mathrm{d}a/\mathrm{d}x$ should be equal to 0.065, 0.12, and 0.18 Å per unit change in x for the S–Se, Se–Te, and S–Te systems, respectively. The corresponding observed values (at low x) are 0.053, 0.10, and 0.12 Å. Clearly, putting tellurium in place of sulfur does not produce as much lateral expansion in the layer as expected.

For the *c* parameter one expects, in addition to expansion due to covalent radius effects on the thickness of the layer, an expansion due to van der Waals radius effects across the gap. We can crudely estimate the gap as being equal to twice the van der Waals radius of the chalcogen, in which case in the mixed systems the gap should expand with x roughly as the difference in van der Waals radii of the two chalcogens involved. Using $r(\mathrm{S}) = 1.80$ Å, $r(\mathrm{Se}) = 1.90$ Å, and $r(\mathrm{Te}) = 2.06$ Å after Bondi[18] and assuming constant bond angles, we calculate $\mathrm{d}c/\mathrm{d}x = 0.16$, 0.22, and 0.32 Å per unit change in x for the S–Se, Se–Te, and S–Te systems, respectively. The corresponding observed values (at low x) are 0.48, 0.84, and 1.59 Å. The expansion is much greater than expected and is especially large when tellurium is being added to the system.

It is tempting to attribute the special action of tellurium to a lone-pair effect, which is fairly prevalent in this region of the periodic table. However, as Gillespie[19] has noted, the lone pair becomes increasingly inert stereochemically as the central core of an atom increases in size. In the layered dichalcogenides, lone-pair stability may be enhanced by exposed nonsymmetrical position of a chalcogen on the outer surface of a layer. A stereochemically active nonbonded pair would have to be in a hybrid orbital. In the simplest view this would be an sp^3 hybrid of the chalcogen, which would be most favored in tellurium (where the 5s and 5p ionization energies are separated by only 8.83 eV) compared to selenium (for 4s–4p, 10.40 eV) and sulfur (for 3s–3p, 9.84 eV).[20] Actually, the situation is more complicated than this in that not only orbital energy differences but also relative sizes of overlap integrals need to be considered. Also, the closer proximity of the *n*d orbitals in the case of tellurium almost certainly means that tellurium d orbitals are involved in the W–Te bonding.

In going from α-WS_2 and α-WSe_2 to β-WTe_2, there is not only a change from trigonal-prismatic to approximately octahedral coordination but there is also a decided change in metallic character. Whereas WS_2 and WSe_2 are semiconductors with band gaps of the order of 0.1 eV, WTe_2 is a semimetal.[21] Starting with a covalent model for WTe_2 and assuming an octahedral environment for the tungsten (the actual distortion is relatively slight), the bonding in WTe_2 can be described as σ covalence between $d_\gamma{}^2sp^3$ hybrids of the W and sp^3 hybrids of the tellurium, overlaid by a conduction band composed of W $5d_\epsilon$ orbitals (with perhaps some Te 5d character). The latter would be unoccupied except for transfer of one-third of an electron from each of the surrounding six Te atoms. The presence of three orbitals for a total of two electrons would be consistent with the metallic character.

The effect of substituting selenium or sulfur for tellurium would be to pull electron density away from the tungsten in the tungsten–chalcogen bond, weaken the incipient W–W bond, and break up any possibility of a W 5d overlap band. It would be interesting to have carrier mobility data for the mixed-anion systems in the tellurium region as a function of departure from exact WTe_2 stoichiometry. The results could clarify the mechanism by which band breakup occurs. It appears that carrier mobility should go from a $T^{-3/2}$ dependence characteristic of acoustic phonon scattering in stoichiometric WTe_2 to an activated-hopping type in the anion-doped systems. Attempts were made in this research to grow large single crystals of the mixed-anion compounds by vapor-phase transport for electrical studies, but ion-probe analysis indicated that stoichiometry was not homogeneous along such a crystal.

Acknowledgment. This research was sponsored by the Air Force Office of Scientific Research (AFSC) under Grant No. AFOSR-74-2583 and was supported in part by the National Science Foundation and the Materials Science Center at Cornell University.

Registry No. WTe_2, 12067-76-4; WS_2, 12138-09-9; WSe_2, 12067-46-8.

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Stability and Electronic Spectra of the Copper(II) Chloro Complexes in Aqueous Solutions

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Received January 22, 1976 AIC60056B

The stability constants and the electronic spectra of the chlorocuprates $CuCl_j^{(j-2)-}$ (with $j \leq 4$) in aqueous solutions of constant 5 M ionic strength have been calculated from spectrophotometric data at 12 wavelengths ranging from 240 to 780 nm. The calculated spectra are compared to those of solid chlorocuprates and solutions in molten salts or organic solvents, in order to get eventual structural information.

Introduction

Aqueous solutions of copper(II) chloro complexes, which absorb in the uv and in the visible regions (λ_{max} ~250 and 800 nm), have mainly been investigated by spectrophotometric methods;[1-14] potentiometric studies are not feasible in Cu(II)–Cl^- media.[15,16]

The main studies at constant ionic strength by uv spectrophotometry are those of McConnel and Davidson,[8] Kruh,[9] Lister and Rosenblum,[1] Wendling et al.,[10] and Libus.[14] The values found for the stability constant β_1 of $CuCl^+$ range from 1 to 3.5, except Kruh's value $\beta_1 = 0.27$ which has been contested by the author himself.

The overall apparent stability constant β_2 of $CuCl_2$ (according to the equation $Cu^{2+} + 2Cl^- \rightleftharpoons CuCl_2$) has only been determined by McConnel and Davidson who found $\beta_2 = 0.30 \pm 0.20$ at ionic strength $\mu = 1$. The overall stability constants β_3 and β_4 have not been determined at all, as the studied media were too poor in chloride ions for any appreciable formation of the $CuCl_3^-$ and $CuCl_4^{2-}$ ions.

One of us (M.J.S.) has recently published the results of the spectrophotometric investigation, at 25 °C, of copper(II) chloro complexes in aqueous solutions of constant ionic strength 5 M containing $NaClO_4$–NaCl mixtures.[17] This high ionic strength was especially chosen in order to promote formation of the most chlorinated complexes. Eventual formation of polynuclear complexes was avoided by always keeping the copper analytical concentration γ lower than the chloride analytical concentration C. Copper hydrolysis was prevented by adjusting the pH of all studied solutions to 2, with perchloric acid.

The optical densities of 37 different solutions with C ranging from 0.005 to 4.9 and γ equal to 6×10^{-4} (up to $C = 0.2$ M) and 6×10^{-3} (for $0.2 < C \leq 4.9$) were measured at six different wavelengths, i.e., 230, 250, 280, 360, 380, and 756 nm.

The matrix rank treatment of Hugus and El-Awady,[18] applied to the measured optical densities, showed unambiguously that a minimum of four chloro complexes have to be taken into account in order to interpret the whole set of data.

Under the chosen experimental conditions, only mononuclear complexes $CuCl_j^{(j-2)-}$ have been considered, e.g., $CuCl^+$, $CuCl_2$, $CuCl_3^-$ and $CuCl_4^{2-}$.

The simultaneous least-squares treatment of the 152 data obtained at 250, 280, 360, 380, and 756 nm leads to the following values of the 95% probability ranges of the overall apparent stability constants $\beta_j = [CuCl_j^{(j-2)-}]/[Cu^{2+}][Cl^-]^j$: β_1 is 3.1–4.9; β_2 is 3.7–5.7; β_3 is 1.26–1.94; β_4 is 0.14–0.17. The given ranges correspond to four times the standard deviations. The central values of the constants, $\beta_1 = 4.0$, $\beta_2 = 4.7$, $\beta_3 = 1.60$, and $\beta_4 = 0.17$, allowed the recalculation within 1% of all the measured optical densities.

We report here the results of our extension of the previous study, made in order to determine the electronic spectra of the four chloro complexes in aqueous solutions. We have measured the optical densities at seven more wavelengths, e.g., 240, 260, 300, 340, 400, 720, and 780 nm, under the same experimental conditions as in the previous work.[17] The stability constants have been refined with the complete set of all experimental data, including those of the previous study (324 experimental data in all, excluding those at 230 nm), and the specific extinction coefficients of each chloro complex at the various wavelengths have been adjusted.

Method of Calculation

At the wavelength λ, the apparent molar extinction coefficient ϵ of a solution of copper(II) analytical concentration γ and chloride analytical concentration C is given by

$$\epsilon - \epsilon_0 = \epsilon' = \frac{\sum_{j=1}^{n} \epsilon_j' c^j \beta_j}{1 + \sum_{j=1}^{n} c^j \beta_j} \qquad (1)$$

where: ϵ_0 is the specific extinction coefficient of the Cu^{2+} ion at wavelength λ; $\epsilon_j' = \epsilon_j - \epsilon_0$; ϵ_j is the specific extinction coefficient of the $CuCl_j^{(j-2)-}$ ion at wavelength λ; c is the free chloride ion concentration; and n is the number of chloro complexes taken into account ($n = 4$).

The unknowns in eq 1 are the β_j, c, and ϵ_j' values (ϵ_0 has been determined experimentally).

The c values for each solution have been calculated by an iterative process, which was stopped either when the difference between the results of two successive iterations was smaller than 10^{-6}, or when the total number of successive iterations exceeded five.[19,20]

For a given set $|\beta_j\rangle$ of β_j values, the sum S^λ of the squares of the relative errors on ϵ' at wavelength λ has been optimized by a least-squares treatment leading to the best ϵ_j' values for the given $|\beta_j\rangle$ set and to the corresponding $S^\lambda(|\beta_j\rangle)$. The total sum $S(|\beta\rangle) = \sum_\lambda S^\lambda(|\beta_j\rangle)$ has then been computed, as well as the standard deviation $\sigma^\lambda(|\beta_j\rangle)$ at wavelength λ

$$\sigma^\lambda(|\beta_j\rangle) = \sqrt{S^\lambda/(N-n)} \qquad (2)$$

N being the number of solutions investigated at wavelength