

Synthesis of Soluble Metal Chalcogenides by the Reduction of Solid State Metal Chalcogenide with Alkali Metal in Liquid Ammonia (I): $K_2(\text{Crypt})_2\text{W}(\text{CO})_4(\text{Te}_2)\cdot\text{CH}_3\text{CN}$

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The use of nontraditional techniques to synthesize chalcogenometalates has led to the isolation of products and conformations usually unobtainable through the more conventional methods of nonaqueous solution chemistry. These nontraditional synthetic methods include cathodic dissolution of electrodes composed of solid-state metal chalcogenide phase,¹ extraction of ternary chalcogenides in ethylenediamine and liquid ammonia,² and solventothermal reactions.³

More recently, chemical reduction method in which a metal chalcogenide is reduced by K in liquid ammonia in the presence of an encapsulating ligand has been used to synthesize various soluble metal chalcogenides. Since the synthesis is carried at low temperature at unique reduction environment, the reaction often produces metal chalcogenide with unusual structures. Encapsulating ligands such as 2.2.2-crypts or crown ethers serve not only to impede electron back donation but also to provide means to alter the cationic size and make the chemistry richer in structures. $[\text{K}(\text{18-crown-6})_4[\text{Cd}_4\text{Te}_2]]$,⁴ $[\text{K}(\text{2.2.2-crypt})_2[\text{Pb}_2\text{Te}_3]]$,⁴ $[(\text{NEt}_4)_5][\text{In}_3\text{Te}_7]$ ⁵ and $[\text{K}(\text{18-crown-6})_2[\text{GaTe}_3]]$ ⁵ are among the representative examples of tellurometalates synthesized by this method.

Metal carbonyls have often been reacted with polytellurides to produce various carbonyl ligand supported tellurometalates.⁶ Since the large size and metallic nature of polytellurides, the coordination of tellurium to metal does not induce the liberation of carbonyl ligands. Therefore, carbonyl ligands are especially useful for synthesizing metal tellurides and selenides. We have used the chemical reduction method of solid metal telluride melt in liquid ammonia combined with utilizing the metal carbonyls to synthesize multi component metal tellurides, and in the course of this attempts, we have synthesized and structurally characterized new metal carbonyl telluride, $K_2(\text{Crypt})_2\text{W}(\text{CO})_4(\text{Te}_2)\cdot\text{CH}_3\text{CN}$.

Experimental Section

Chemical and Reagents. All manipulations were carried out under Ar atmosphere with the use of standard Schlenk techniques. Solvents were distilled, dried, and degassed before use. Anhydrous diethyl ether was purchased from Aldrich Chemical Co. Korea and was distilled over Na/benzophenone. Acetonitrile was purchased from Aldrich Chemical Co. Korea and was distilled over CaH_2 . Ammonia gas (anhydrous, 99.95 purity) was purchased from Linde Gas Corp. 2.2.2-Cryptand (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane) was dissolved in acetonitrile and

was recrystallized by evaporation. The remaining reagents were purchased from Aldrich Chemical Co. Korea and were used as received.

Synthesis of $K_2(\text{Crypt})_2\text{W}(\text{CO})_4(\text{Te}_2)\cdot\text{CH}_3\text{CN}$. Melt of nominal composition CuAsTe was prepared by fusing stoichiometric amount of the powders of constituent elements in fused silica tubes with H_2/O_2 flame under argon atmosphere. The melt was finely ground before use. NH_3 (60 mL) was condensed into a flask containing 2.2.2-cryptand (221 mg, 0.394 mmol) and K (44 mg, 1.12 mmol) at liquid N_2 temperature (-195°C). The resulting blue solution was stirred at -78°C and all the K dissolved. Finely ground CuAsTe melt (50 mg, 0.188 mmol) was added with stirring and the solution turned red after 30 min. The solution was stirred at -78°C for 12 hour and $\text{W}(\text{CO})_6$ (66 mg, 0.188 mmol) was added and stirring was continued for additional 1 hour. Color of solution changed to red brown. NH_3 was allowed to evaporate at room temperature. After the residue was extracted with 30 mL of degassed acetonitrile, the extract was filtered. Layering 50 mL of degassed ether on the filtrate yielded after 1 week dark red brown crystals which were characterized as $K_2(\text{Crypt})_2\text{W}(\text{CO})_4(\text{Te}_2)\cdot\text{CH}_3\text{CN}$ by X-ray single crystallography. Yield: 53 mg (19.8% based on tungsten). IR. Nujol mull (cm^{-1}): $\nu(\text{CO}) = 1977(\text{m}), 1956(\text{m}), 1915(\text{s, br}), 1844(\text{s, br}), 1823(\text{w})$.

X-ray Single-Crystal Structure Determination. A dark red brown single crystal of dimensions $0.21 \times 0.21 \times 0.11 \text{ mm}^3$ was mounted on a thin glass fiber. Diffraction data were collected on a Siemens SMART CCD diffractometer⁷ equipped with a normal focus, 2 kW sealed tube X-ray source and graphite monochromated $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at 193(2) K. The intensity data collected with increasing ω (width of 0.3° per frame) covered one hemisphere of the reciprocal space. Data reduction and absorption correction was carried out with the programs SAINT⁸ and SADABS,⁹ respectively. The intensities were corrected for Lorentz and polarization effects. The structure was solved by direct methods and refined on F^2 by full-matrix least squares using SHELXTL¹⁰ program in the triclinic space group $P\bar{1}$. All non-hydrogen atoms were refined either isotropically or anisotropically. No hydrogen atoms were located but were placed geometrically and refined in the riding mode of the carbon atoms of crypt and acetonitrile. The complete data collection parameters and details of the structure solution and refinement are given in Table 1. The final atomic coordinates, temperature factors, and their esti-

Table 1. Crystal data and structure refinement for $K_2(\text{Crypt})_2\text{W}(\text{CO})_4(\text{Te}_2)\cdot\text{CH}_3\text{CN}$

| | | |
|-----------------------------------|--|----------------------------|
| Empirical formula | $K_2(\text{Crypt})_2\text{W}(\text{CO})_4(\text{Te}_2)\cdot\text{CH}_3\text{CN}$ | |
| Formula weight | 1423.32 | |
| Temperature | 193(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Triclinic | |
| Space group | $P\bar{1}$ | |
| Unit cell dimensions | $a = 11.138(3)$ Å | $\alpha = 95.61(2)^\circ$ |
| | $b = 12.574(5)$ Å | $\beta = 102.46(2)^\circ$ |
| | $c = 21.363(6)$ Å | $\gamma = 104.10(3)^\circ$ |
| Volume | $2797.4(15)$ Å ³ | |
| Z | 2 | |
| Density (calculated) | 1.690 Mg/m ³ | |
| Absorption coefficient | 3.301 mm ⁻¹ | |
| F(000) | 1412 | |
| Crystal size | 0.21 × 0.21 × 0.11 mm ³ | |
| Theta range for data collection | 0.99 to 26.52° | |
| Index ranges | -4 ≤ h ≤ 13, -14 ≤ k ≤ 11, -26 ≤ l ≤ 26 | |
| Reflections collected | 7928 | |
| Independent reflections | 7914 [R(int) = 0.0575] | |
| Completeness to theta = 26.52° | 68.1% | |
| Refinement method | Full-matrix least-squares on F ² | |
| Data/restraints/parameters | 7914/0/593 | |
| Goodness-of-fit on F ² | 1.213 | |
| Final R indices [I > 2σ(I)] | R1 = 0.1051, wR2 = 0.2060 | |
| R indices (all data) | R1 = 0.1560, wR2 = 0.2408 | |
| Largest diff. peak and hole | 1.960 and -3.213 e.Å ⁻³ | |

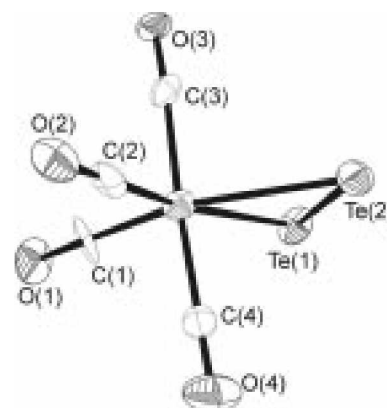
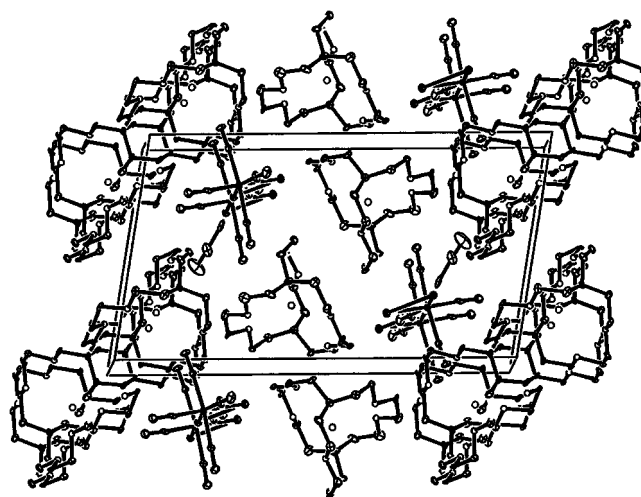
Table 2. Atomic coordinates ($\times 10^1$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) of selected atoms for $K_2(\text{Crypt})_2\text{W}(\text{CO})_4(\text{Te}_2)\cdot\text{CH}_3\text{CN}$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor

| | x | y | z | U (eq) |
|-------|----------|----------|----------|--------|
| W(1) | 7487(1) | 2439(1) | 2385(1) | 29(1) |
| Te(2) | 10100(1) | 2776(1) | 2332(1) | 36(1) |
| Te(1) | 9411(1) | 2041(2) | 3411(1) | 39(1) |
| O(1) | 5122(15) | 2049(16) | 2982(8) | 58(5) |
| O(2) | 5826(15) | 2901(14) | 1128(8) | 45(5) |
| O(3) | 6734(14) | -68(17) | 1694(9) | 40(5) |
| O(4) | 8317(18) | 5012(17) | 2910(9) | 57(5) |
| C(1) | 6008(19) | 2190(20) | 2752(10) | 41(7) |
| C(2) | 6500(20) | 2754(18) | 1608(12) | 33(6) |
| C(3) | 7050(20) | 840(30) | 1965(12) | 30(8) |
| C(4) | 8020(20) | 4080(20) | 2723(12) | 30(5) |

mated standard deviations are given in Table 2.

Results and Discussion

$K_2(\text{Crypt})_2\text{W}(\text{CO})_4(\text{Te}_2)\cdot\text{CH}_3\text{CN}$ was isolated from the reductive dissolution of multi components CuAsTe melt by K in $\text{NH}_3(\text{l})$ in the presence of 2,2,2-cryptand followed by reaction with tungsten hexacarbonyl. CuAsTe is an intimate mixture of Cu, As and Te elements with 1 : 1 : 1 ratio. For the reduction by K in $\text{NH}_3(\text{l})$, the use of alkali metal sequestering agent is crucial, since encapsulation of the cation helps to prevent tight-ion pairing that otherwise would cause reversion of the compounds formed to insoluble materials.

**Figure 1.** Ortep representation of the $[\text{W}(\text{CO})_4(\text{Te}_2)]^{2-}$ anion containing four terminal carbonyl ligands and $\eta^2\text{-Te}_2^{2-}$ chelating ligand to complete octahedral coordination environment of W. (50% ellipsoid probability).**Figure 2.** Ortep representation of the packing diagram of $K_2(\text{Crypt})_2\text{W}(\text{CO})_4(\text{Te}_2)\cdot\text{CH}_3\text{CN}$ composed of $[\text{K}(\text{Crypt})]^+$ cations and $[\text{W}(\text{CO})_4(\text{Te}_2)]^{2-}$ anions and space filling acetonitrile CH_3CN solvent molecules with a labeling scheme. (carbon atoms represented as boundary ellipsoids are not labeled for clarity) (40% ellipsoid probability).

The sequestering reagent also provides larger cationic species that help the large anionic metal telluride crystallize. Although no multi components metal telluride could be successfully isolated in this system, new tungsten carbonyl telluride $K_2(\text{Crypt})_2\text{W}(\text{CO})_4(\text{Te}_2)\cdot\text{CH}_3\text{CN}$ has been isolated and structurally characterized.

The $[\text{W}(\text{CO})_4(\text{Te}_2)]^{2-}$ anion contains four terminal carbonyl ligands and $\eta^2\text{-Te}_2^{2-}$ chelating ligand to complete octahedral coordination environment of W as shown in Figure 1. The structure of $K_2(\text{Crypt})_2\text{W}(\text{CO})_4(\text{Te}_2)\cdot\text{CH}_3\text{CN}$ comprises of $[\text{K}(\text{Crypt})]^+$ cation and $[\text{W}(\text{CO})_4(\text{Te}_2)]^{2-}$ anions and space filling acetonitrile CH_3CN solvent molecule as shown in Figure 2. Mononuclear complexes containing $\eta^2\text{-Te}_2^{2-}$ ligands are rare, and the only structurally characterized tungsten complex of which we are aware of is $\text{W}(\text{PMe}_3)_4(\text{OCN}^t\text{Bu})_4(\eta^2\text{-Te}_2)$ (where Me = methyl and Bu^t = tert-butyl).¹¹ The Te-Te distance in chelating Te_2^{2-} unit is 2.757(2) Å and it is inter-

mediate between those of Te_2 in the gas phase [2.59(2) Å]¹² and elemental Te_x in the solid state [2.835(2) Å]¹³ and is slightly longer than that in $\text{W}(\text{PMe}_3)(\text{OCNBu})_4(\eta^2\text{-Te}_2)$ [2.680(2) Å].¹¹ The W-Te bond distances at 2.866(2) and 2.892(2) Å are compared well with those of the other known tungsten-tellurium compounds.^{6,14} The bond angle of $\text{Te}(1)\text{-W-Te}(2)$ is restrained to 57.21deg due to the chelating nature of the Te_2^{2-} ligand resulting in distorted octahedral coordination environment of W metal ion. There are two-types of W-CO bond distances based on the relative position of terminal carbonyl ligands compared to Te ligands. The W-CO bond distances, trans to Te, are 1.91(2)-1.95(2) Å whereas those *cis* to Te, are slightly longer at 2.01(3)-2.02(3) Å. This may be understood in terms of more efficient back π bond formation of W metal to the carbonyl ligands trans to Te rather than to the carbonyl ligands *cis* to Te. This is consistent with the fact that the bond C-O distances (1.18(2)-1.19(2) Å) trans to the Te are slightly longer than those (1.15(3)-1.16(3) Å) *cis* to Te. It is important to note that the low electron density of tungsten metal center due to effective back π bond formation stabilize low oxidation state and prevent the oxidative addition of $\eta^2\text{-Te}_2$ ligand to metal to form two terminal telluride ligands.¹¹ K^+ ions are encapsulated by 6 oxygen atoms of the crypt in the charge compensating $[\text{K}(\text{Crypt})]^+$ units. These are quite common and the K-O bond distances are found normal at 2.76(1)-2.89(2) Å. Other selected bond distances and angles are given in Table 3.

In this paper we have shown the chemical reduction method of solid metal telluride melt in liquid ammonia combined with utilizing the metal carbonyl compound to synthesize multi component soluble metal tellurides. We have synthesized and structurally characterized new metal carbonyl telluride, $\text{K}_2(\text{Crypt})_2\text{W}(\text{CO})_4(\text{Te}_2)\cdot\text{CH}_3\text{CN}$. Other carbonyl ligand supported multi component new metal chalcogenide compounds are being synthesized using this method.

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Supplementary Material Available: Tables of the atomic coordinates and anisotropic thermal parameters of all non-hydrogen atoms, and a listing of calculated and observed ($10F_o/F_c$) structure factors. These supporting materials will be given upon the request to the correspondence author. (Tel: +82-42-821-1546, Fax: +82-42-821-1593, E-mail: parkc@hyunam.tnut.ac.kr)

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Table 3. Selected bond lengths [Å] and angles [°] for $\text{K}_2(\text{Crypt})_2\text{W}(\text{CO})_4(\text{Te}_2)\cdot\text{CH}_3\text{CN}$

| | | | |
|------------------|------------|------------------|------------|
| W(1)-C(1) | 1.945(19) | W(1)-C(2) | 1.91(2) |
| W(1)-C(3) | 2.02(3) | W(1)-C(4) | 2.01(3) |
| W(1)-Te(1) | 2.8918(19) | W(1)-Te(2) | 2.8660(18) |
| Te(2)-Te(1) | 2.757(2) | O(1)-C(1) | 1.18(2) |
| O(2)-C(2) | 1.19(2) | O(3)-C(3) | 1.16(3) |
| O(4)-C(4) | 1.15(3) | | |
| C(1)-W(1)-C(4) | 92.4(9) | C(1)-W(1)-C(3) | 93.2(9) |
| C(1)-W(1)-Te(1) | 101.9(5) | C(1)-W(1)-Te(2) | 158.7(6) |
| C(2)-W(1)-C(1) | 90.5(8) | C(2)-W(1)-C(4) | 87.8(9) |
| C(2)-W(1)-C(3) | 89.2(9) | C(2)-W(1)-Te(1) | 167.6(6) |
| C(2)-W(1)-Te(2) | 110.4(6) | C(3)-W(1)-Te(2) | 91.2(5) |
| C(3)-W(1)-Te(1) | 89.8(6) | C(4)-W(1)-C(3) | 173.7(8) |
| C(4)-W(1)-Te(2) | 84.6(6) | C(4)-W(1)-Te(1) | 92.0(6) |
| Te(2)-W(1)-Te(1) | 57.21(5) | Te(1)-Te(2)-W(1) | 61.87(5) |
| Te(2)-Te(1)-W(1) | 60.92(5) | | |