

# [Me<sub>4</sub>N]<sub>3</sub>[(WOS<sub>3</sub>)<sub>2</sub>Ag]·MeCN – An Acetonitrile Solvate with Linear Complex Anions

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*Dedicated to Professor Wolfgang Jeitschko on the occasion of his 70<sup>th</sup> birthday*

The title compound was prepared by the reaction of [Me<sub>4</sub>N]<sub>2</sub>WOS<sub>3</sub> with AgCN in MeCN at room temperature and slow crystallisation in the refrigerator. It was characterized by IR and mass spectroscopy. It crystallizes in the orthorhombic space group *Pnma* (No. 62) with unit cell dimensions  $a = 19.648(7)$ ,  $b = 27.878(12)$ ,  $c = 11.494(3)$  Å,  $Z = 8$ . The crystal structure was determined from single crystal diffractometer data (Mo-K $\alpha$  radiation) and refined to  $R = 0.077$ . The structure is composed of mixed double layers containing the linear trinuclear anion [(WOS<sub>3</sub>)<sub>2</sub>Ag]<sup>3-</sup> and cations separated by a layer formed by cations and solvating acetonitrile molecules.

**Key words:** [Me<sub>4</sub>N]<sub>3</sub>[(WOS<sub>3</sub>)<sub>2</sub>Ag]·MeCN, Chalcogenide Complex, Mass Spectrum, Crystal Structure

## Introduction

In two earlier papers we described the formation of [Me<sub>4</sub>N]<sub>3</sub>[(TOS<sub>3</sub>)<sub>2</sub>Ag] ( $T = \text{Mo, W}$ ) [1] and of polymeric [Me<sub>4</sub>N]<sub>4</sub>[(WOS<sub>3</sub>Ag)<sub>2</sub>] [2] by reaction of the corresponding oxotrithiometalates with AgCN. Experiments to isolate the binuclear complex [Me<sub>4</sub>N]<sub>2</sub>[(WOS<sub>3</sub>AgCN)] resulted in the crystallization of the title compound.

## Experimental Section

### Preparation

To a suspension of [Me<sub>4</sub>N]<sub>2</sub>WOS<sub>3</sub> (0.200 g, 0.4501 mmol) in 40 ml of MeCN, an equimolar amount of solid AgCN (0.0301 g, 0.4496 mmol) was added. The colour of the solution changed from yellow to orange yellow and the previously turbid solution became almost clear. Stirring was continued for 1 h, and the solution was filtered. The filtrate was kept in the refrigerator for slow crystallization. Yellow needle-shaped crystals of the title compound deposited within one week. The isolated crystals were air sensitive and kept under vaseline in order to avoid decomposition. A qualitative test was positive for silver. The crystals were characterized by infrared and mass spectroscopy and by single crystal X-ray analysis and were formulated as [Me<sub>4</sub>N]<sub>3</sub>[(WOS<sub>3</sub>)<sub>2</sub>Ag]·MeCN.

Table 1. Crystallographic Data for [Me<sub>4</sub>N]<sub>3</sub>[(WOS<sub>3</sub>)<sub>2</sub>Ag]·MeCN.

<i>a</i>	19.648(7) Å
<i>b</i>	27.878(12) Å
<i>c</i>	11.494(3) Å
Space group	<i>Pnma</i> (No. 62)
<i>Z</i>	8
<i>V</i>	6296(3) Å <sup>3</sup>
<i>d<sub>x</sub></i>	2.045 g cm <sup>-3</sup>
<i>M<sub>r</sub></i>	969.46
$\mu(\text{Mo-K}\alpha)$	83.3 cm <sup>-1</sup>
<i>F</i> (000)	3712.0
<i>Structure refinement:</i>	
<i>h, k, l</i> Range	$0 \leq h \leq 25, 0 \leq k \leq 35, 0 \leq l \leq 14$
Unique reflections	5615
Observed reflections	3166
Cutoff	$3\sigma(I)$
Variables	96
$R = \Sigma  F_o  -  F_c   / \Sigma F_o $	0.077
$Rw = [\Sigma w  F_o  -  F_c  ^2 / \Sigma w F_o ^2]^{1/2}$	0.141
$w = [\sigma(F_o^2)^2 + (0.005F_o^2)^2]^{-1/2}$	
Residual electron density	2.85 / -3.04 eÅ <sup>-3</sup>

### Infrared spectrum

IR spectra were recorded from powder in KBr using a Bio-Rad FTS-45 FTIR spectrophotometer. The following most important spectral lines are:  $\tilde{\nu} = 3015$  (C-H, s), 1482 (H<sub>3</sub>C-N, vs), 948 (bending H<sub>3</sub>C-N, vs), 902 (termi-

Table 2. Positional parameters and equivalent isotropic temperature factors for [Me<sub>4</sub>N]<sub>3</sub>[(WOS<sub>3</sub>)<sub>2</sub>Ag] · MeCN.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>eq</sub> <sup>a</sup>
W(1)	0.22943(4)	0.11038(3)	0.82728(7)	3.95(2)
W(2)	0.04713(4)	0.10083(3)	0.23730(7)	3.76(2)
Ag	0.14057(9)	0.11109(7)	0.0367(2)	5.07(4)
S(1)	0.3123(3)	0.1516(3)	0.7514(7)	6.8(2)
S(2)	0.2614(3)	0.0803(3)	0.9968(6)	6.0(2)
S(3)	0.1378(3)	0.1567(3)	0.8421(5)	5.0(2)
S(4)	0.9532(3)	0.1366(3)	0.2781(8)	7.6(2)
S(5)	0.1308(3)	0.1545(3)	0.2283(6)	5.5(2)
S(6)	0.0365(3)	0.0577(3)	0.0763(6)	5.7(2)
O(1)	0.211(1)	0.064(1)	0.741(2)	9.3(7)
O(2)	0.062(1)	0.063(1)	0.351(1)	7.4(5)
N(1)	0.295(1)	1/4	0.074(3)	4.4(6)
N(2)	0.973(1)	1/4	0.984(3)	4.6(7)
N(3)	0.288(1)	0.067(1)	0.411(2)	4.1(4)
N(4)	0.991(1)	0.074(1)	0.655(1)	3.8(4)
N(5)	0.267(2)	1/4	0.454(3)	11.2(2)
N(6)	0.005(2)	1/4	0.618(4)	8.6(1)
C(1)	0.230(2)	1/4	0.030(7)	14(2)
C(2)	0.308(3)	0.294(1)	0.140(4)	15(2)
C(3)	0.332(4)	1/4	0.996(9)	23(5)
C(4)	0.047(2)	1/4	0.018(7)	17(3)
C(5)	0.955(2)	0.293(2)	0.927(4)	15(2)
C(6)	0.936(3)	1/4	0.100(5)	17(3)
C(7)	0.295(2)	0.121(1)	0.432(3)	10(1)
C(8)	0.340(2)	0.045(1)	0.484(3)	10(1)
C(9)	0.293(2)	0.055(1)	0.287(3)	9(1)
C(10)	0.220(1)	0.055(2)	0.456(3)	10(1)
C(11)	0.936(1)	0.057(1)	0.586(3)	7.2(8)
C(12)	0.005(2)	0.123(1)	0.622(3)	7.9(9)
C(13)	0.973(1)	0.070(1)	0.780(2)	6.1(7)
C(14)	0.054(1)	0.046(1)	0.635(3)	8.2(9)
C(15)	0.238(2)	1/4	0.531(4)	6(1)
C(16)	0.026(2)	1/4	0.526(4)	6(1)
C(17)	0.201(2)	1/4	0.648(4)	8(1)
C(18)	0.051(3)	1/4	0.397(4)	8(1)

$$^a B_{eq} = \frac{8\pi^2}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \mathbf{a}_j.$$

nal W–O, vs), 873 (terminal W–O, m), 477 (terminal W–S, s), 433 (bridging W–S, vs) cm<sup>−1</sup>.

#### Mass spectrum

Mass spectra were obtained from MeCN solution using a quadrupole system HP5989B equipped with an atmosphere pressure ionization interface HP55987A and a RF-only hexapole (Analytica Brandford). Data were collected for the cations and anions of the complex compound using two different programs. The following peaks were observed: for anions: *m/z* 700 for [(WOS<sub>3</sub>)<sub>2</sub>Ag]<sup>−</sup>, *m/z* 668 for [(WOS<sub>3</sub>)(WOS<sub>2</sub>)Ag]<sup>−</sup>, *m/z* 468 for [(WOS<sub>3</sub>)AgS<sub>2</sub>]<sup>−</sup>, *m/z* 404 for [WOS<sub>3</sub>Ag]<sup>−</sup>, *m/z* 296 for [WOS<sub>3</sub>]<sup>−</sup>; for the cation: *m/z* 74 for [Me<sub>4</sub>N]<sup>+</sup>.

#### Crystal structure determination

The crystals obtained directly from the preparation were suitable for single crystal X-ray work. For the structure de-

Table 3. Selected bond lengths (Å) and angles (°) in the anion [(WOS<sub>3</sub>)<sub>2</sub>Ag]<sup>3−</sup>.

W1	O1	1.67(2)	S1	W1	O1	109.7(8)°
W1	S1	2.175(6)	S1	W1	S2	109.9(3)°
W1	S2	2.213(7)	S1	W1	S3	109.3(3)°
W1	S3	2.223(6)	S2	W1	O1	106.6(9)°
W1	Ag	2.974(2)	S2	W1	S3	112.5(2)°
			S3	W1	O1	108.7(8)°
W2	O2	1.71(2)	S4	W2	O2	105.7(6)°
W2	S4	2.149(7)	S4	W2	S5	109.4(3)°
W2	S5	2.226(6)	S4	W2	S6	110.7(3)°
W2	S6	2.218(6)	S5	W2	O2	109.1(7)°
W2	Ag	2.961(2)	S5	W2	S6	113.3(2)°
			S6	W2	O2	108.4(7)°
Ag	S2	2.566(6)	S2	Ag	S3	91.7(2)°
Ag	S3	2.574(6)	S2	Ag	S5	112.8(2)°
Ag	S5	2.520(7)	S2	Ag	S6	125.0(3)°
Ag	S6	2.571(6)	S3	Ag	S5	121.4(2)°
			S3	Ag	S6	115.0(2)°
			S5	Ag	S6	93.7(2)°

termination a well developed plate-like crystal with the dimensions 0.25 × 0.15 × 0.10 mm was selected and embedded with vaseline into a thin walled glass capillary. All measurements were made using a Nonius Turbo CAD4 four-circle Kappa diffractometer with graphite monochromated Mo-K<sub>α</sub> radiation (λ = 0.71707 Å). The intensity data were collected at 21(1)° C using the ω – 2θ scan technique to a maximum 2θ value of 49.9°. Omega scans of several intense reflections, made prior to data collection with take off angle 2.8° and scan width (0.8 + 0.35 tan θ)°.

The structure was solved by using direct methods (SIR92) [3] and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically. The final cycle of full matrix least-squares refinement on F was based on 3166 observed reflections and 334 variable parameters and converged with unweighted and weighted agreement factors of *R*1 = 0.077 and *wR*2 = 0.141. All calculations were performed using programs of the MolEN software package [4]. An empirical method [5] was applied to account for absorption effects. Crystallographic data and details of the structure refinement are presented in Table 1. The atomic parameters and equivalent isotropic displacement parameters are shown in Table 2, selected atomic distances and bond angles in Table 3. Further details on the structure determination and anisotropic displacement parameters have been deposited with the Cambridge crystallographic data Centre under the deposition no. CCDC 609672 (E-mail: deposit@ccdc.cam.ac.uk).

## Results and Discussions

### Preparation

It can be assumed that the [(WOS<sub>3</sub>)<sub>2</sub>Ag]<sup>3−</sup> anion results from substitution of the cyanide ligand in primar-

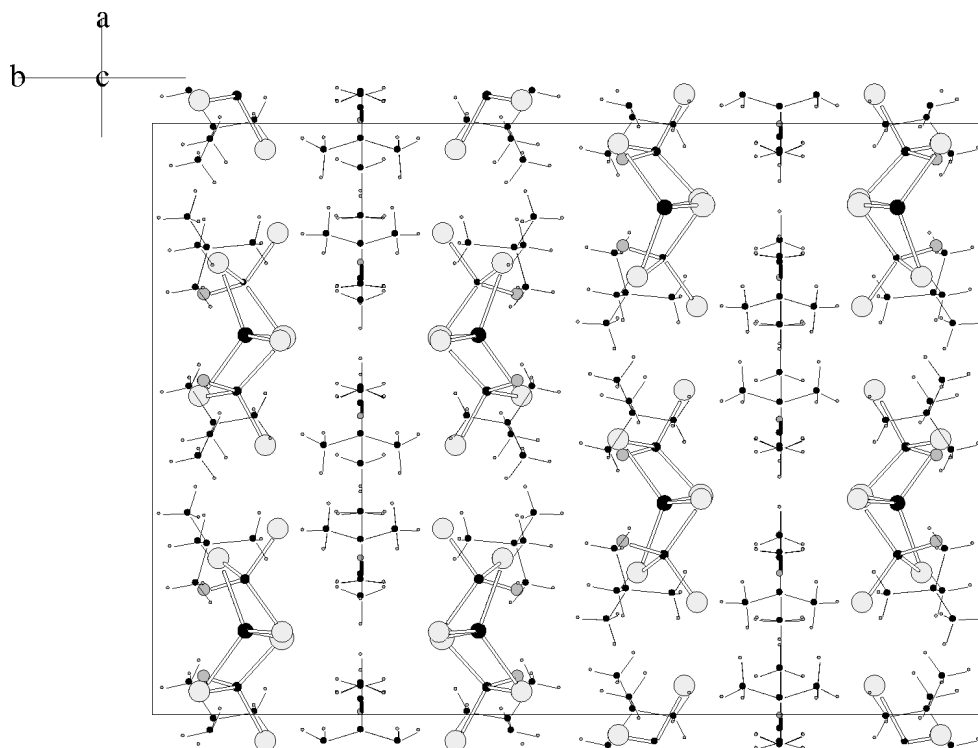


Fig. 1. The crystal structure of [Me<sub>4</sub>N]<sub>3</sub>[(WOS<sub>3</sub>)<sub>2</sub>Ag] · MeCN seen along the *c*-axis.

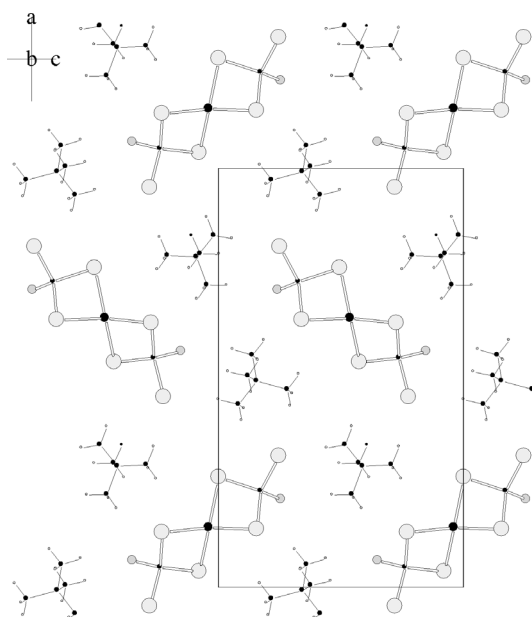


Fig. 2. Mixed layer of composition [(Me<sub>4</sub>N)<sub>2</sub>(WOS<sub>3</sub>)<sub>2</sub>Ag]<sup>−</sup>.

ily formed [(WOS<sub>3</sub>)AgCN]<sup>2−</sup> by a second chelating (WOS<sub>3</sub>)<sup>2−</sup> entity. Indeed, [(WOS<sub>3</sub>)AgCN]<sup>−</sup> has been

detected by mass spectroscopy in the reaction solution [2].

#### *Infrared spectrum*

The infrared spectrum of the complex does not display any band in the region between 2200–2000 cm<sup>−1</sup>, suggesting that cyanide groups might not be present in the complex. The absorption bands corresponding to the terminal  $\tilde{\nu}(\text{W-O})$  stretching vibrations at 902 (vs) and 873 (ms) cm<sup>−1</sup> indicate that the complex has a terminal W-O group [1, 2, 6]. The strong bands found at 477 and 433 cm<sup>−1</sup> were assigned to terminal  $\tilde{\nu}(\text{W-S})$  and bridging  $\tilde{\nu}(\text{W-S})$  stretching modes [6]. Additional bands at 3015, 1482 and 948 cm<sup>−1</sup> are assigned to  $\tilde{\nu}(\text{C-H})$ ,  $\tilde{\nu}(\text{H}_3\text{C-N})$  and bending ( $\text{H}_3\text{C-N})$  modes, respectively, of the tetramethylammonium cation.

#### *Mass spectrum*

The anionic mass spectrum showed a molecular ion peak at  $m/z$  700 for [(WOS<sub>3</sub>)<sub>2</sub>Ag]<sup>−</sup>. Other peaks found in the spectrum

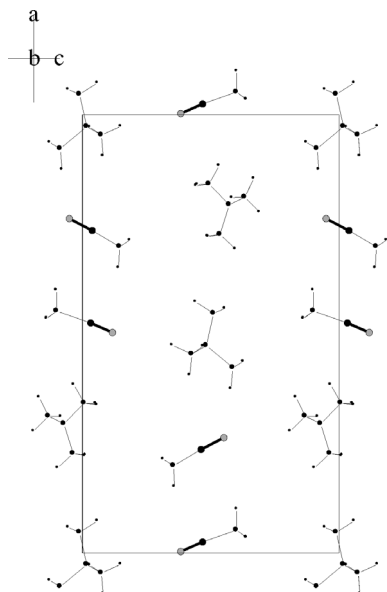


Fig. 3. Mixed layer of composition [(Me<sub>4</sub>N)<sub>2</sub> · (MeCN)<sub>2</sub>]<sup>2+</sup>.

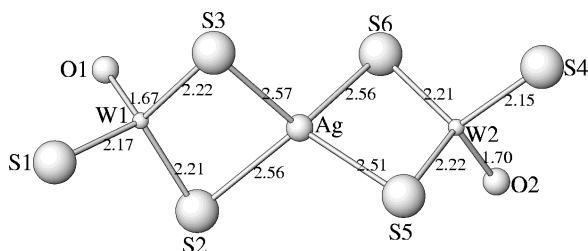


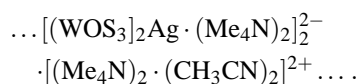
Fig. 4. Atom labelling and bond distances in the [(WOS<sub>3</sub>)<sub>2</sub>Ag]<sup>3-</sup> anion.

at  $m/z$  668 for [(WOS<sub>3</sub>)(WOS<sub>2</sub>)Ag]<sup>-</sup>,  $m/z$  468 for [(WOS<sub>3</sub>)AgS<sub>2</sub>]<sup>-</sup>,  $m/z$  404 for [WOS<sub>3</sub>Ag]<sup>-</sup>, and  $m/z$  296 for [WOS<sub>3</sub>]<sup>-</sup> fragments suggest that the fragmentation proceeds from one side of the molecule by losing successively masses of one S, one WO, two S and finally Ag. The same fragmentation pattern was also found in the mass spectrum of the same

anion in solvate-free [Me<sub>4</sub>N]<sub>3</sub>[(WOS<sub>3</sub>)<sub>2</sub>Ag] [1] as one should expect.

### Crystal structure

The crystal structure (Fig. 1) is composed of layers parallel to the *ac* plane. There are four mixed layers per unit cell formed by the complex anions and [Me<sub>4</sub>N]<sup>+</sup> cations in a ratio 1 : 2. In each layer the linear [(WOS<sub>3</sub>)<sub>2</sub>Ag]<sup>3-</sup> anions are arranged alternately in diagonal orientations with [Me<sub>4</sub>N]<sup>+</sup> cations in between (Fig. 2). Two layers are relatively close together thus forming a double layer. These double layers are separated by a mixed layer of solvating acetonitrile molecules and tetramethylammonium ions in a ratio 1 : 1 (Fig. 3). Thus the structure can be described as a stacking of formally charged layers



The complex anion is formed by 3 edge-linked tetrahedra with Ag in the centre (Fig. 4). The two oxygen atoms are terminal and by geometry in a staggered position to each other. Contrary to the coordination of the tungsten atoms the tetrahedral coordination of the silver atom is distorted. The most significant interatomic distances and angles in the anion are shown in Table 3.

It is interesting that the crystal structure of the title MeCN solvate is very different from that of [Me<sub>4</sub>N]<sub>3</sub>[(MoOS<sub>3</sub>)<sub>2</sub>Ag] and from that of the isotypic tungsten compound, where the [(TOS<sub>3</sub>)<sub>2</sub>Ag]<sup>3-</sup> anions are stacked one above the other forming channels in which the [Me<sub>4</sub>N]<sup>+</sup> cations are accommodated [1].

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