UPR-RP
Inorganic Chemistry
Dr. Arthur D. Tinoco
December 1, 2016

Antimony
Properties, Uses, and Applications

Carolina Rojas Michea
Wilfredo J. Cardona Vélez
Robert A. Vélez Peña
José A. Méndez Román

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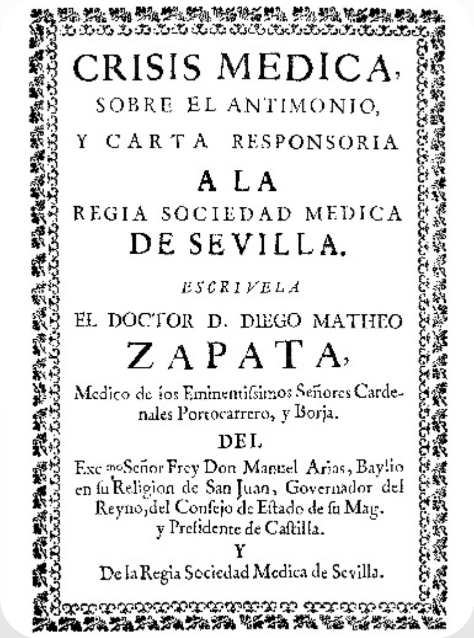
Introduction: History



CRISIS MEDICA,
SOBRE EL ANTIMONIO,
Y CARTA RESPONSORIA
A LA
REGIA SOCIEDAD MEDICA
DE SEVILLA.
ESCRIVELA
EL DOCTOR D. DIEGO MATHEO
ZAPATA,
Medico de los Eminentiſsimos Señores Cardenales Portocarrero, y Borja.
DEL
Exc.mo Señor Frey Don Manuel Arias, Baylio en ſu Religion de San Juan, Governador del Reyno, del Conſejo de Eſtado de ſu Mag. y Preſidente de Caſtilla.
Y
De la Regia Sociedad Medica de Sevilla.

http://www.cervantesvirtual.com/obra-visor/crisis-medica-sobre-el-antimonio-y-carta-responsoria-a-la-regia-sociedad-medica-de-sevilla--0/html/ff0e6e6e-82b1-11df-acc7-002185ce6064_2.htm#1
http://www.camimex.org.mx/index.php/secciones1/sala-de-prensa/uso-de-los-metales/antimonio/
https://berbellin.wordpress.com/2010/05/31/el-buda-de-oro/
https://quimimol.wikispaces.com/Antimonio+-+Un+veneno+muy+musical

Introduction: Antimony

^{121}Sb
57.25%

22 isotopes

^{123}Sb
42.74%

15/VA

51 121,75
+3,5

Sb

$5s^2 5p^3$

- ✓ MP 630.2 ^oC
- ✓ BP 1750 ^oC
- ✓ d 6691 kgm^{-3}
- ✓ TC 24.40 $mm^{-1}s^{-1}{}^oC^{-1}$
- ✓ EC 25.6 $mOhmcm^{-1}$

Exposure

Intake

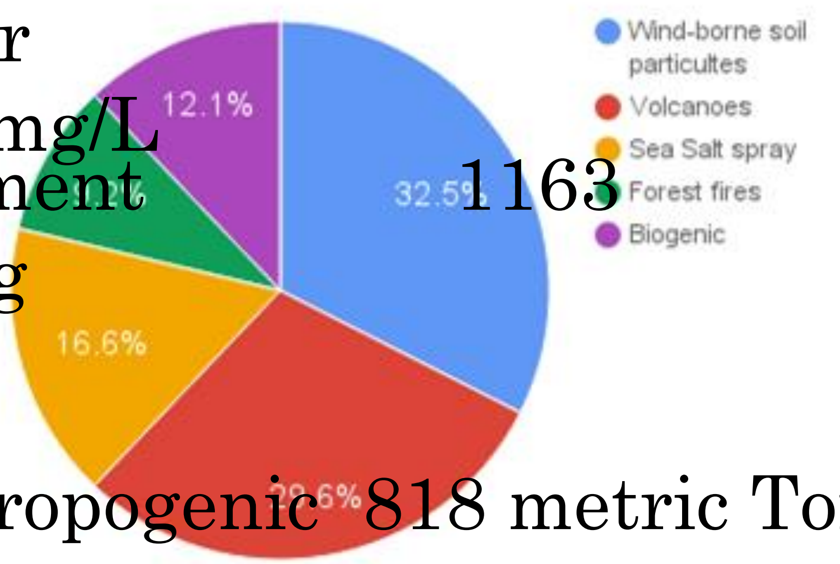
- Food
    - Food ready-table
- Water
- Milk

Environment

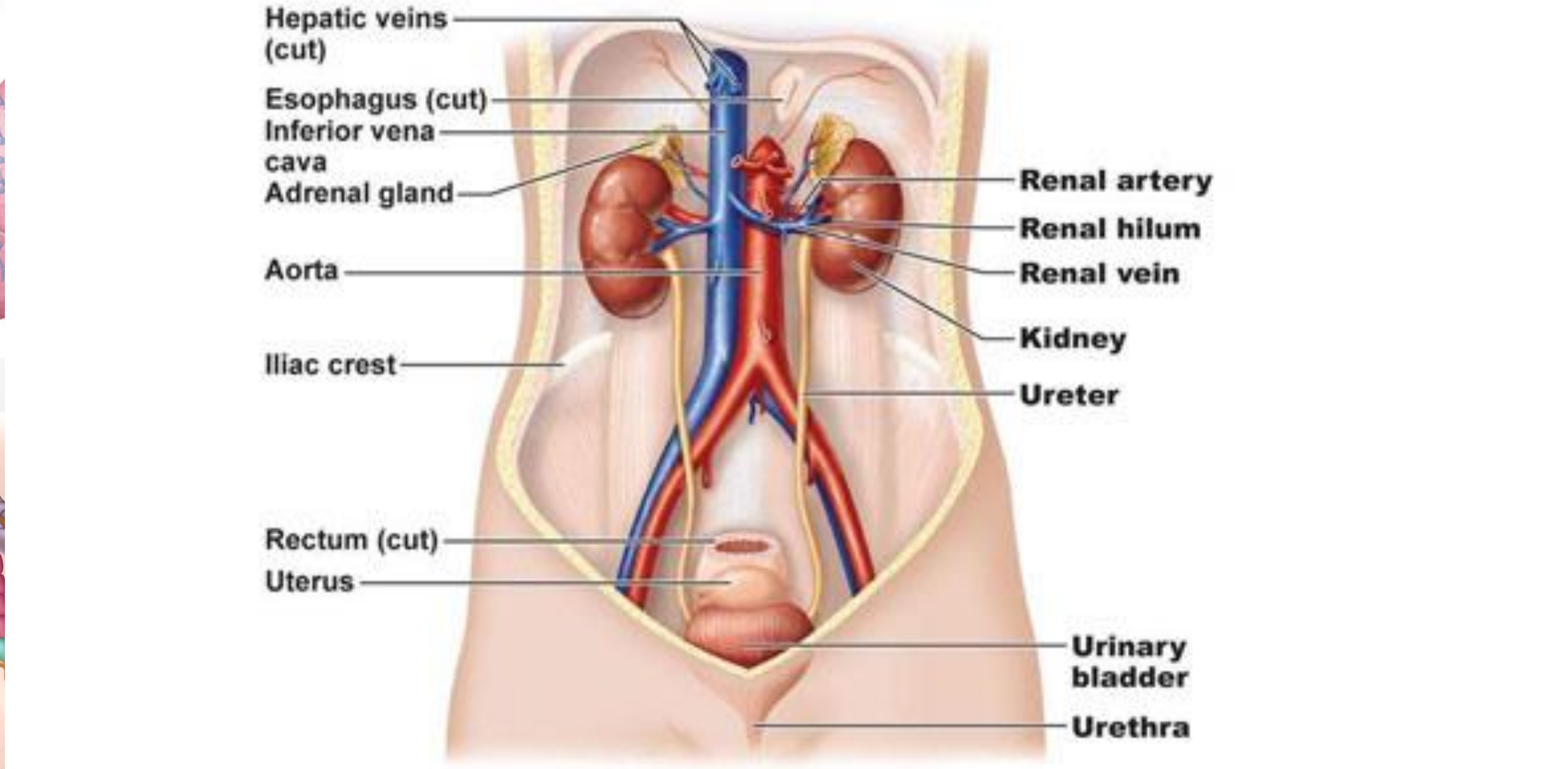
Water 29.4 mg/L

Sediment 1163 mg/kg

Anthropogenic Activities 818 metric Ton



Exposure: Elimination



https://sites.google.com/site/functionsofthehumanbodysystems/urinary-system
http://ponteensalud.net/2016/02/07/estos-son-algunos-remedios-caseros-para-limpiar-y-desintoxicar-sus-pulmones/
http://www.dmedicina.com/enfermedades/urologicas/2002/04/04/son-calculos-renales-7421.html
http://www.lavidalucida.com/5-senales-de-que-tienes-un-intestino-perforado.html

Periodic Table of Elements

1 IA 1A	2 IIA 2A	3 IIIB 3B	4 IVB 4B	5 VB 5B	6 VIB 6B	7 VIIB 7B	8	9 VIII 8	10	11 IB 1B	12 IIB 2B	13 IIIA 3A	14 IVA 4A	15 VA 5A	16 VIA 6A	17 VIIA 7A	18 VIIIA 8A
1 H Hydrogen 1.008																	2 He Helium 4.003
3 Li Lithium 6.941	4 Be Beryllium 9.012											5 B Boron 10.811	6 C Carbon 12.011	7 N Nitrogen 14.007	8 O Oxygen 15.999	9 F Fluorine 18.998	10 Ne Neon 20.180
11 Na Sodium 22.990	12 Mg Magnesium 24.305											13 Al Aluminum 26.982	14 Si Silicon 28.086	15 P Phosphorus 30.974	16 S Sulfur 32.066	17 Cl Chlorine 35.453	18 Ar Argon 39.948
19 K Potassium 39.098	20 Ca Calcium 40.078	21 Sc Scandium 44.956	22 Ti Titanium 47.867	23 V Vanadium 50.942	24 Cr Chromium 51.996	25 Mn Manganese 54.938	26 Fe Iron 55.845	27 Co Cobalt 58.933	28 Ni Nickel 58.693	29 Cu Copper 63.546	30 Zn Zinc 65.38	31 Ga Gallium 69.723	32 Ge Germanium 72.631	33 As Arsenic 74.922	34 Se Selenium 78.971	35 Br Bromine 79.904	36 Kr Krypton 84.798
37 Rb Rubidium 84.468	38 Sr Strontium 87.62	39 Y Yttrium 88.906	40 Zr Zirconium 91.224	41 Nb Niobium 92.906	42 Mo Molybdenum 95.95	43 Tc Technetium 98.907	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.906	46 Pd Palladium 106.42	47 Ag Silver 107.868	48 Cd Cadmium 112.411	49 In Indium 114.818	50 Sn Tin 118.711	51 Sb Antimony 121.760	52 Te Tellurium 127.6	53 I Iodine 126.904	54 Xe Xenon 131.294
55 Cs Cesium 132.905	56 Ba Barium 137.328	57-71	72 Hf Hafnium 178.49	73 Ta Tantalum 180.948	74 W Tungsten 183.84	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.217	78 Pt Platinum 195.085	79 Au Gold 196.967	80 Hg Mercury 200.592	81 Tl Thallium 204.383	82 Pb Lead 207.2	83 Bi Bismuth 208.980	84 Po Polonium [208.982]	85 At Astatine 209.987	86 Rn Radon 222.018
87 Fr Francium 223.020	88 Ra Radium 226.025	89-103	104 Rf Rutherfordium [261]	105 Db Dubnium [262]	106 Sg Seaborgium [266]	107 Bh Bohrium [264]	108 Hs Hassium [269]	109 Mt Meitnerium [268]	110 Ds Darmstadtium [269]	111 Rg Roentgenium [272]	112 Cn Copernicium [277]	113 Uut Ununtrium unknown	114 Fl Flerovium [289]	115 Uup Ununpentium unknown	116 Lv Livermorium [298]	117 Uus Ununseptium unknown	118 Uuo Ununoctium unknown

Lanthanide Series	57 La Lanthanum 138.905	58 Ce Cerium 140.116	59 Pr Praseodymium 140.908	60 Nd Neodymium 144.243	61 Pm Promethium 144.913	62 Sm Samarium 150.36	63 Eu Europium 151.964	64 Gd Gadolinium 157.25	65 Tb Terbium 158.925	66 Dy Dysprosium 162.500	67 Ho Holmium 164.930	68 Er Erbium 167.259	69 Tm Thulium 168.934	70 Yb Ytterbium 173.055	71 Lu Lutetium 174.967
Actinide Series	89 Ac Actinium 227.028	90 Th Thorium 232.038	91 Pa Protactinium 231.036	92 U Uranium 238.029	93 Np Neptunium 237.048	94 Pu Plutonium 244.064	95 Am Americium 243.061	96 Cm Curium 247.070	97 Bk Berkelium 247.070	98 Cf Californium 251.080	99 Es Einsteinium [254]	100 Fm Fermium 257.095	101 Md Mendelevium 258.1	102 No Nobelium 259.101	103 Lr Lawrencium [262]

Characteristics: Antimony vs 5A Family

Common 5A Heavy metal Behavior

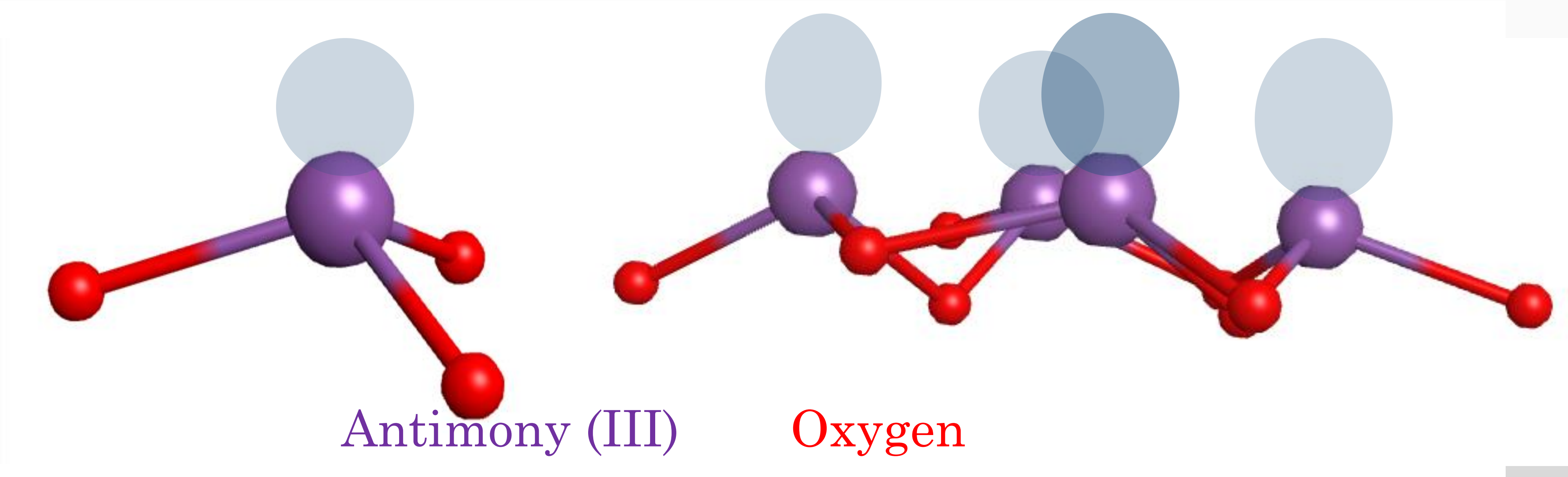
- Oxidation State of V
- Molecular arrangement of mostly Trigonal pyramidal

Antimony behavior

- Common Oxidation State of (III), Although the Oxidation State of (V) is possible.
- Different molecular arrangements: Trigonal pyramidal, octahedral

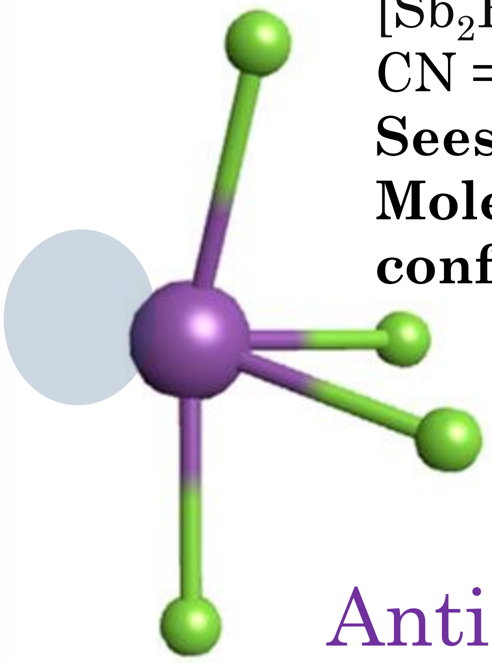
Antimony's Structures

- Antimony trigonal pyramidal molecular arrangement for $Sb_2O_{6.}$ Coordination Number (CN) = 3

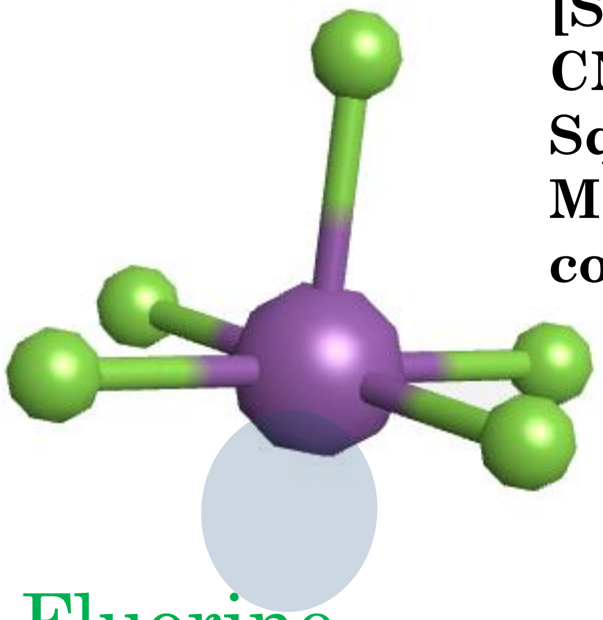


Antimony's Structures

- Common geometrical structures for antimony are:



$[Sb_2F_7]^-$
CN = 4
Seesaw
Molecular
configuration

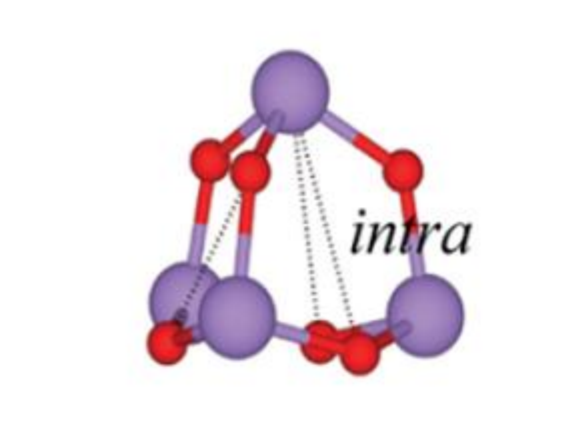


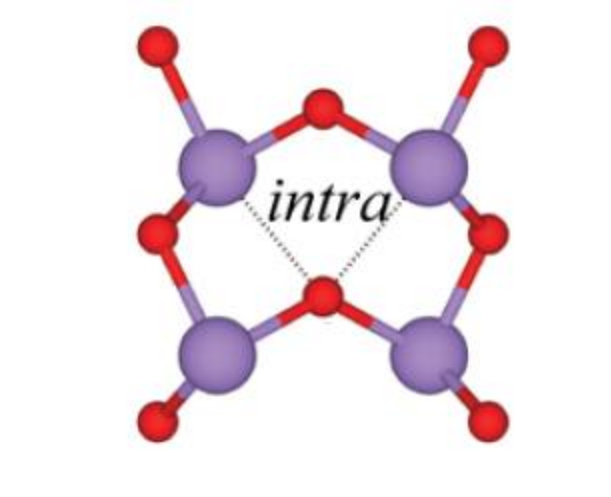
$[SbF5]^-$
CN= 5
Square Pyramidal
Molecular
configuration

Antimony (III), Fluorine

Complex Formations

- Which geometry type would be expected to have an oxide of antimony (III), Sb_2O_6 ?Oxigen, Antimony (III)

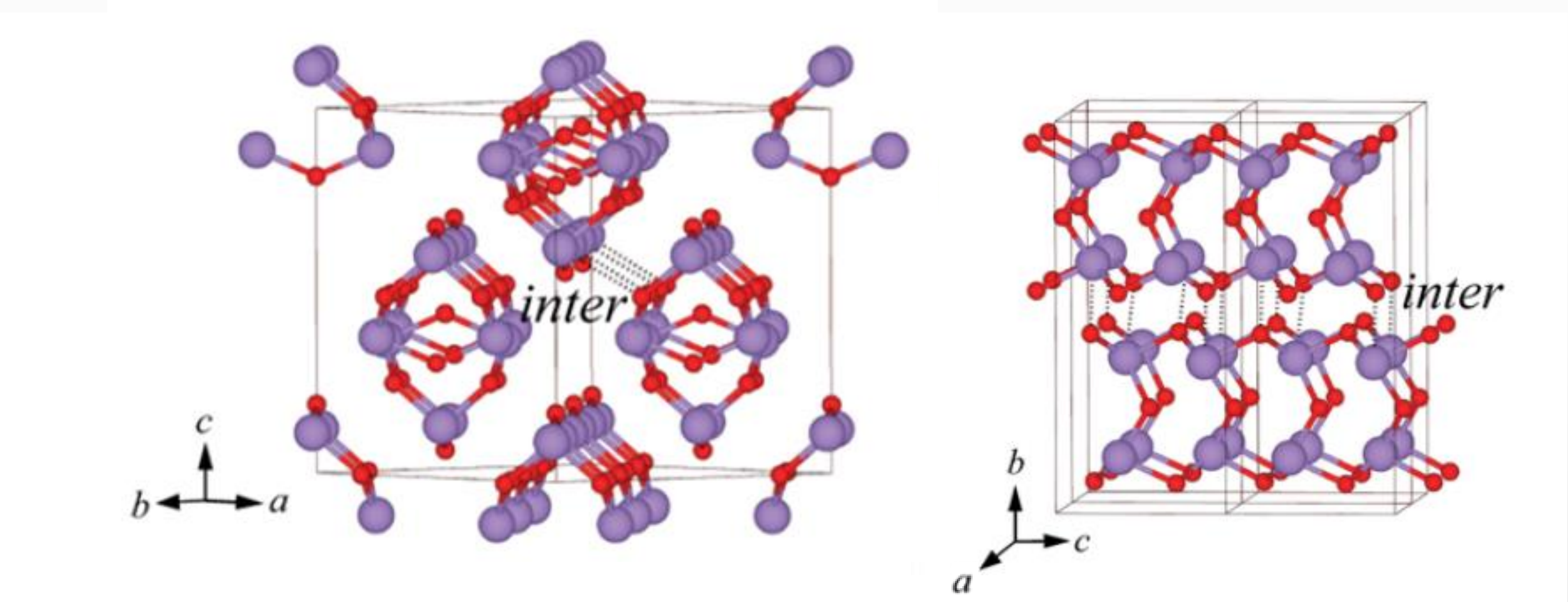




Allen, J P., Carey, J. J., Walsh A., Scanlon D. O., Watson G. W., Electronic Structures of Antimony Oxides, The Journal of Chemical Physical Chemistry C 2013, 117, 14759−14769

Complex Formations

- What type of lattice the antimony oxide can be expected?

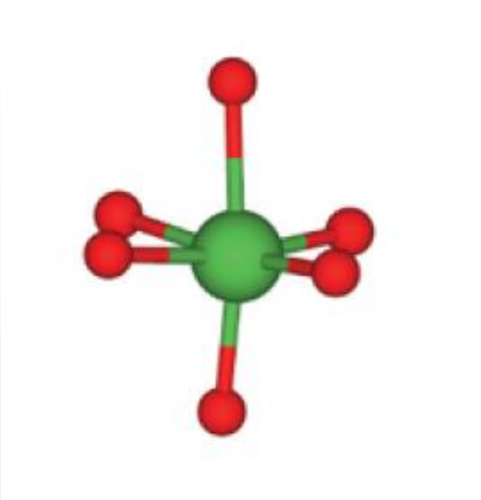


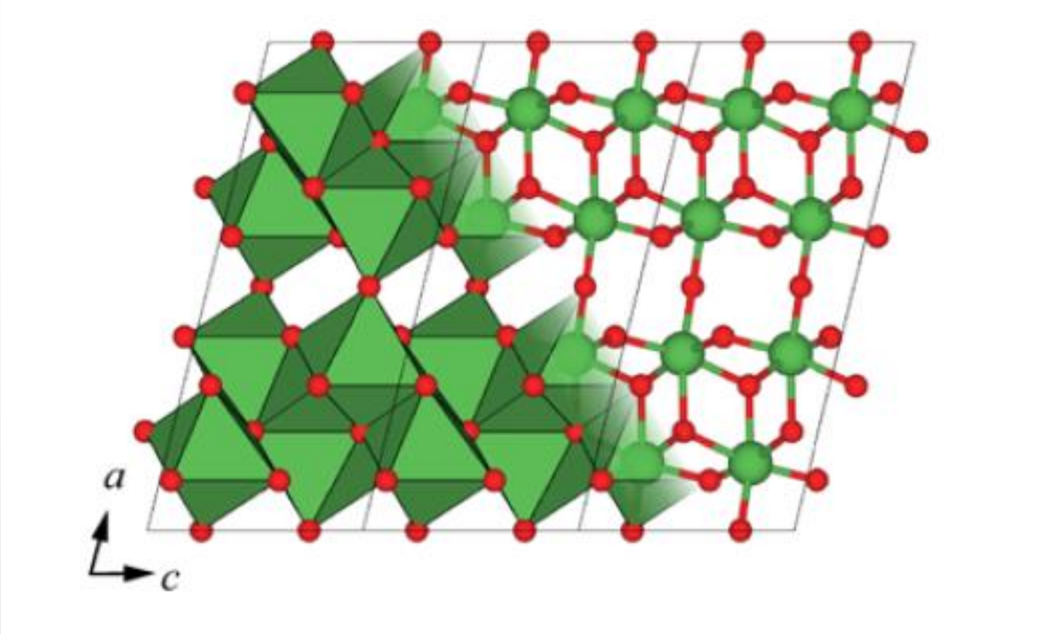
Allen, J P., Carey, J. J., Walsh A., Scanlon D. O., Watson G. W., Electronic Structures of Antimony Oxides, The Journal of Chemical Physical Chemistry C 2013, 117, 14759–14769

Complex Formations

- What type of geometry would be expected to have an oxide of antimony (V) and its' lattice? Antimony (V)

CN = 6

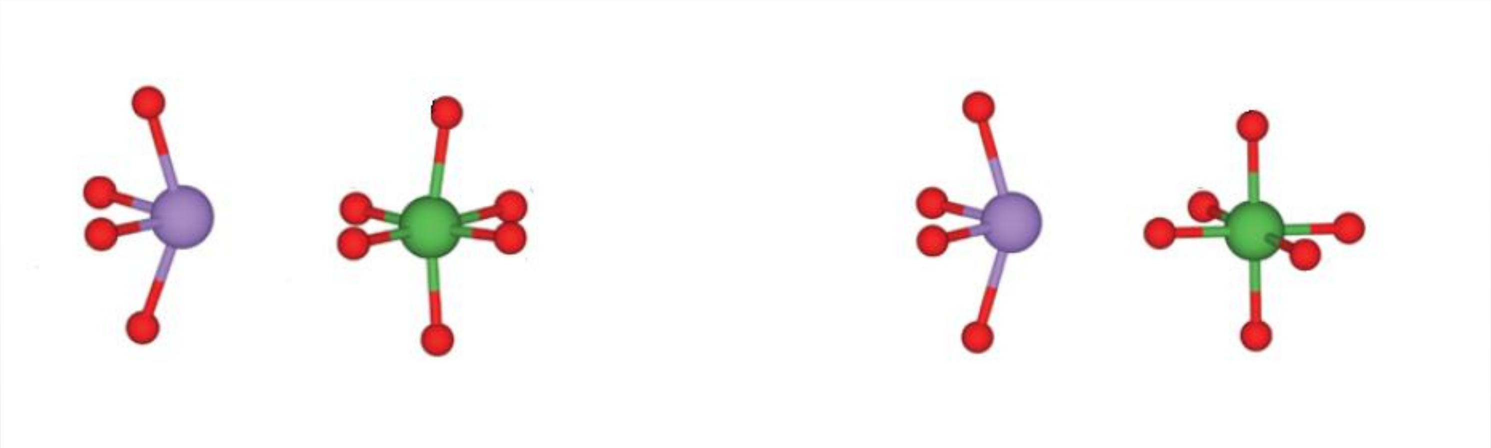




Allen, J P., Carey, J. J., Walsh A., Scanlon D. O., Watson G. W., Electronic Structures of Antimony Oxides, The Journal of Chemical Physical Chemistry C 2013, 117, 14759–14769

Complex Formations

- What would be required for an oxide antimony (IV) geometry to take place?



- What type of geometry should be expected or observed from an oxide of antimony (IV) ?

Complex Formations

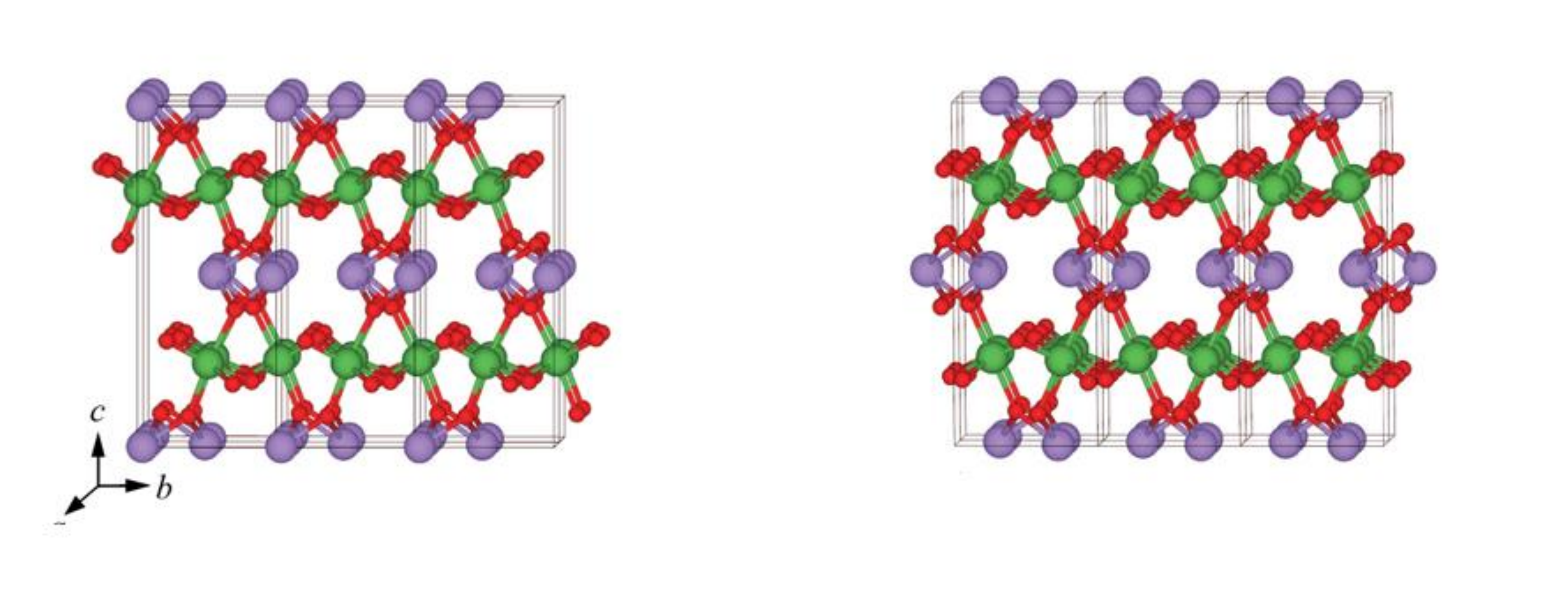
- The crystals of an oxide of Sb(IV) are composed by a proportional amount of 1:1 Sb(III) and Sb(V),

But does not have an actual Sb(IV) atom

Allen, J P., Carey, J. J., Walsh A., Scanlon D. O., Watson G. W., Electronic Structures of Antimony Oxides, The Journal of Chemical Physical Chemistry C 2013, 117, 14759−14769

Complex Formations

Therefore, the lattices for the antimony (IV) oxide, would undergo into different crystal packing. The observed ones are α(left) and β(left):



Allen, J P., Carey, J. J., Walsh A., Scanlon D. O., Watson G. W., Electronic Structures of Antimony Oxides, The Journal of Chemical Physical Chemistry C 2013, 117, 14759–14769

Applications

- Chemical Industry
  - Retardant flame
  - Metal alloy
  - Explosives
  - Electrode analytical
  - Semiconductor
- Biological
  - Drug
- Catalyst


Accessed (11/17/2016)
https://www.google.com/search?q=Industry&espv=2&biw=1600&bih=721&source=lnms&tbm=isch&sa=X&ved=0ahUKEwjInOqQkrHQAhUDeSYKHUBYCF4Q_AUICCgD#imgrc=_gGSgq7grxFscM%3A
https://www.google.com/search?q=pills&espv=2&biw=1600&bih=721&site=webhp&source=lnms&tbm=isch&sa=X&ved=0ahUKEwixt9-0krHQAhUK6iYKHZ93AVwQ_AUIBigB#imgrc=1NWcRqrjiQZqdM%3A

Sb_2O_3 – Flame Retardant

Free Radicals in a Combustion Cycle

H● + O2 ↔HO● +O●

O● + H2 ↔HO● +O●

HO● + CO ↔CO_2 +H●

Flame Retardant Main Reactions

MX → HX + M●

MX + H● → HX + M●

HO● +HX→ H_2O+ X●

M, Metal; X, Halogen

Flame Retardant Conclusion

- Used on cloth, wood, and other fabrics

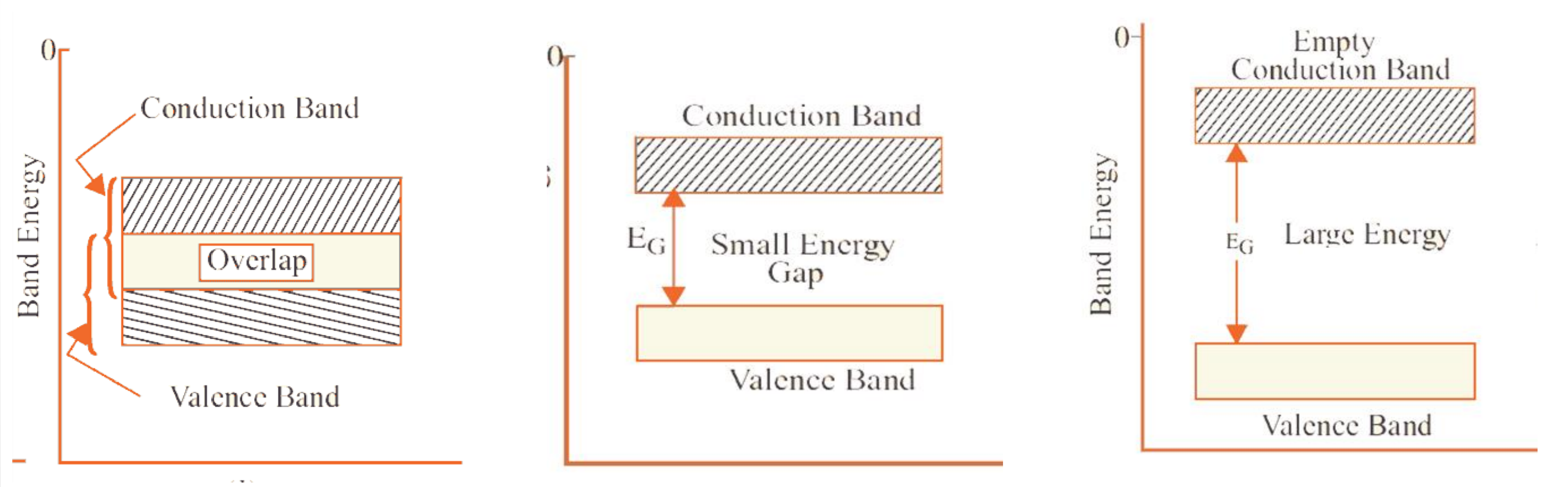
- Industrial manufacturing purposes

- Applied on paints

http://www.svmag.co.za/articlepage.php?cp=107

Photovoltaic Devices (PVD)

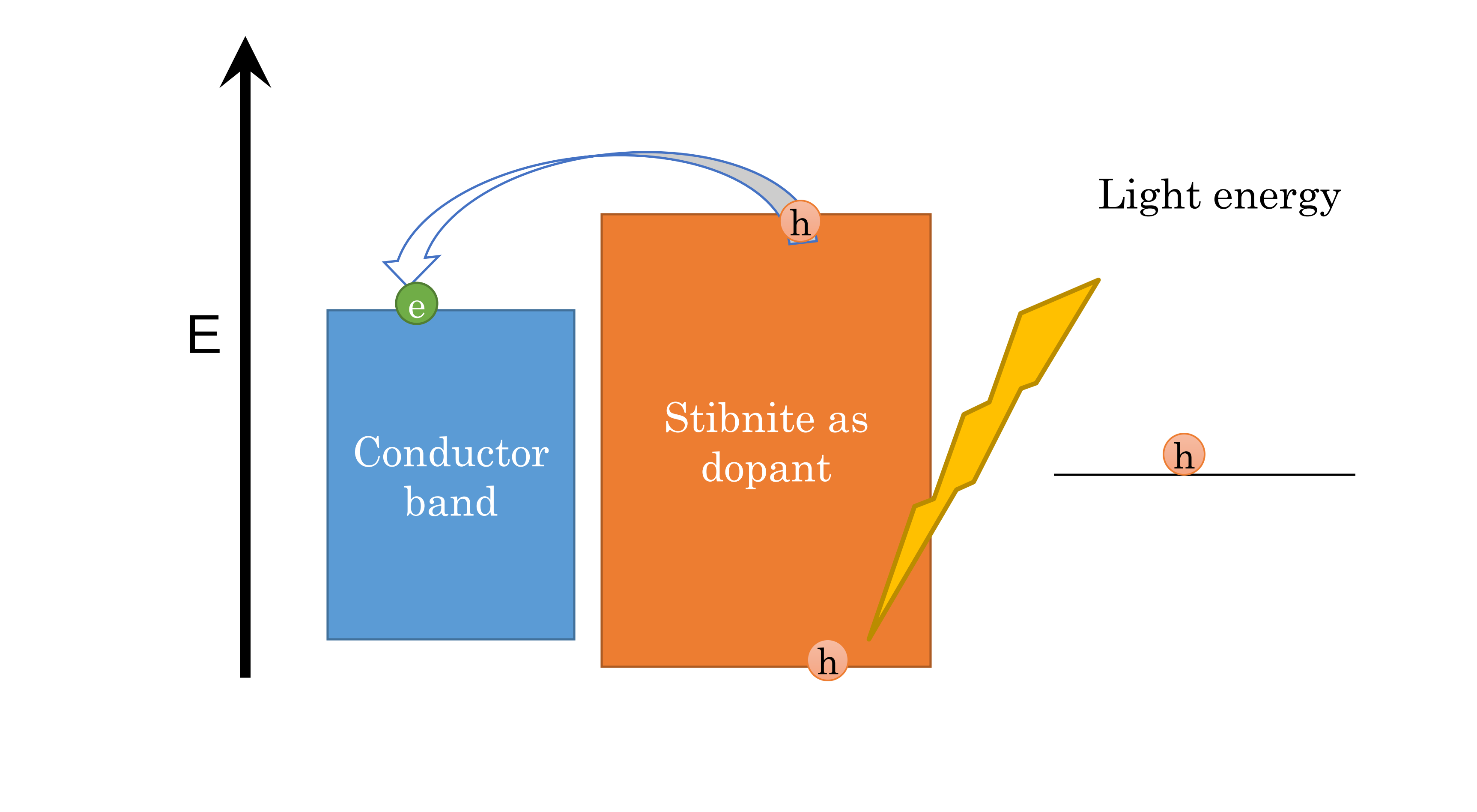
- Conversion of light into electricity with the use of semiconducting materials



Conductor **Semiconductor** **Insulator**

http://www.studyelectrical.com/2015/05/insulators-conductors-and.html

Sb Derivatives in a PVD Energy Diagram



$$\eta = \frac{P}{E * A}$$

η= Efficiency
η_{max} = 46.0%

P= output power

E= incident photonic power

A= incident area of E

Guijarro, N., Lutz, T., Lana-Villarreal T.,‡ O'Mahony, F., Gómez, R.,‡ Haque, S. A., Toward Antimony Selenide Sensitized Solar Cells: Efficient Charge Photogeneration at spiro-OMeTAD/Sb2Se3/Metal Oxide Heterojunctions, J. Phys. Chem. Lett. 2012, 3, 1351−1356

Antimony Facts Summary in PVD

- Antimony Oxides had been notice to have a good behavior to be used as p type semiconductor.

- Other compound used as a semiconductor is Stibnite (Sb_2S_3) with an eficiency of 6.2%

What is metal alloys?

- Mixture of two of more substances with at least one will be a metal element.
- Alloying changes the physical, resistance to corrosion, heat, and other properties of the material to fit a given job.

Examples:

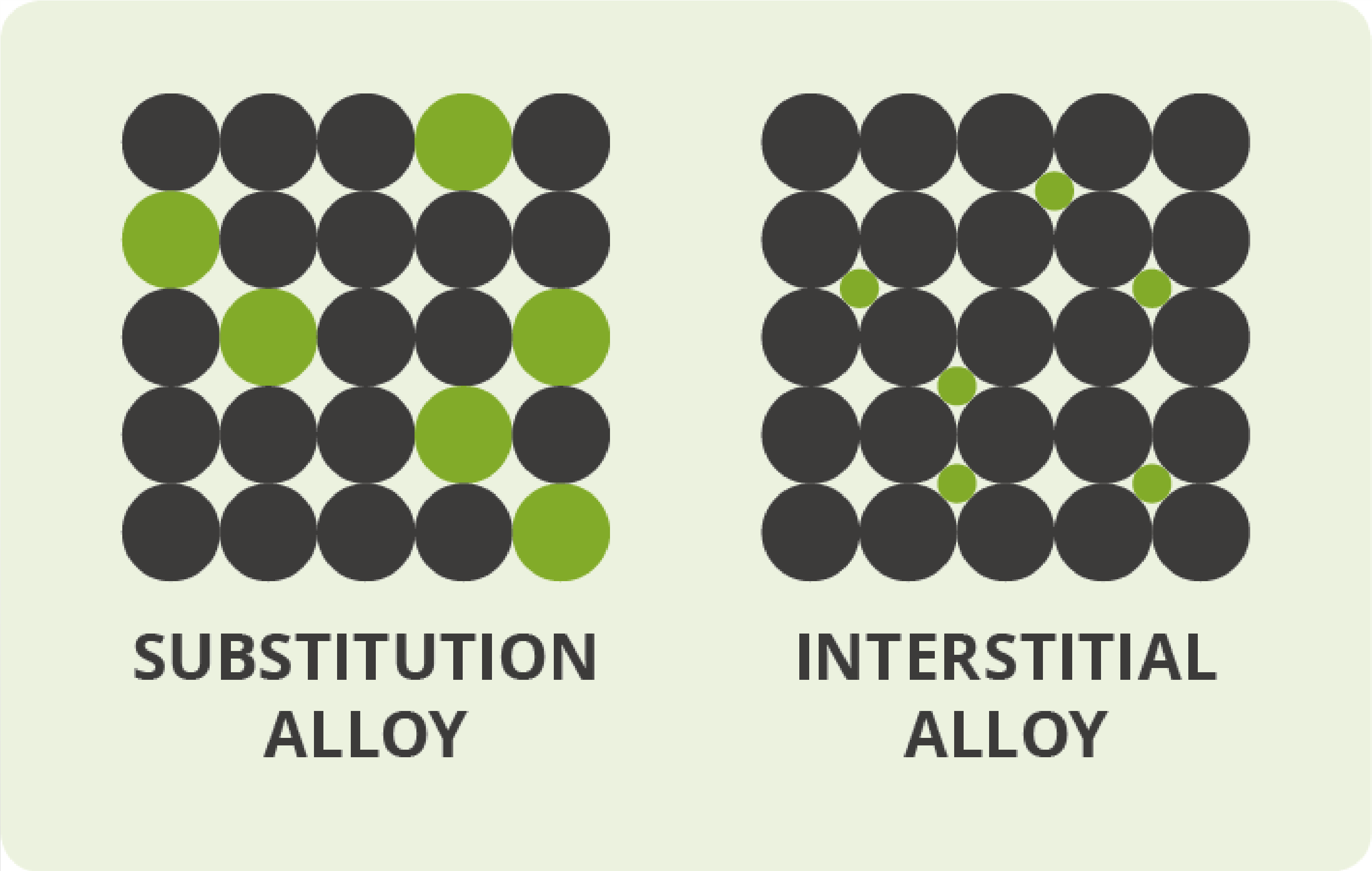
Bronze

Gold for Jewerly

Steel

http://www.studentsollution.com/alloys/

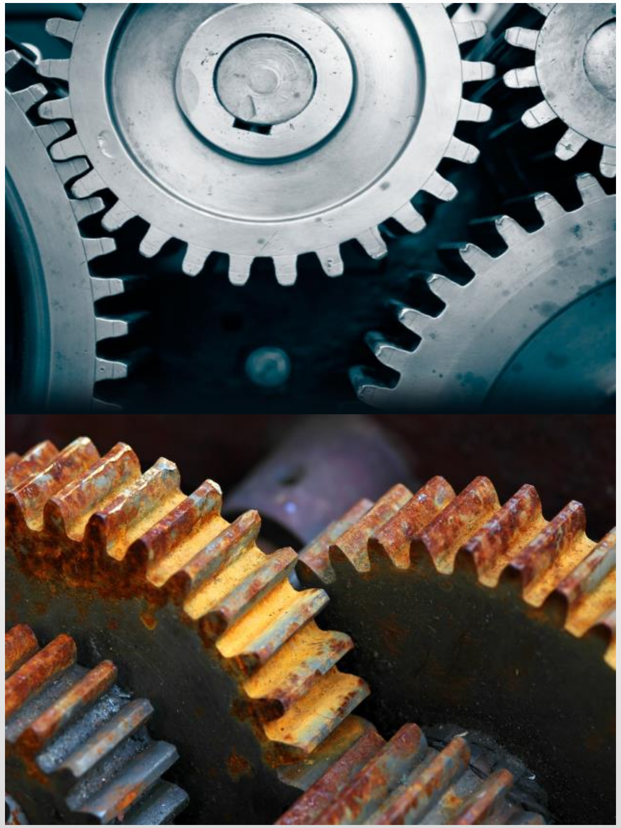
Types of metal alloys



http://www.compoundchem.com/2015/07/07/alloys/

General Sb Alloy Benefits

- Macro properties:
  - Increasing hardness on metals
  - Resistant to wearness
  - Antifriction
- Micro properties:
  - Corrosion resistant
  - Photosensitive usages

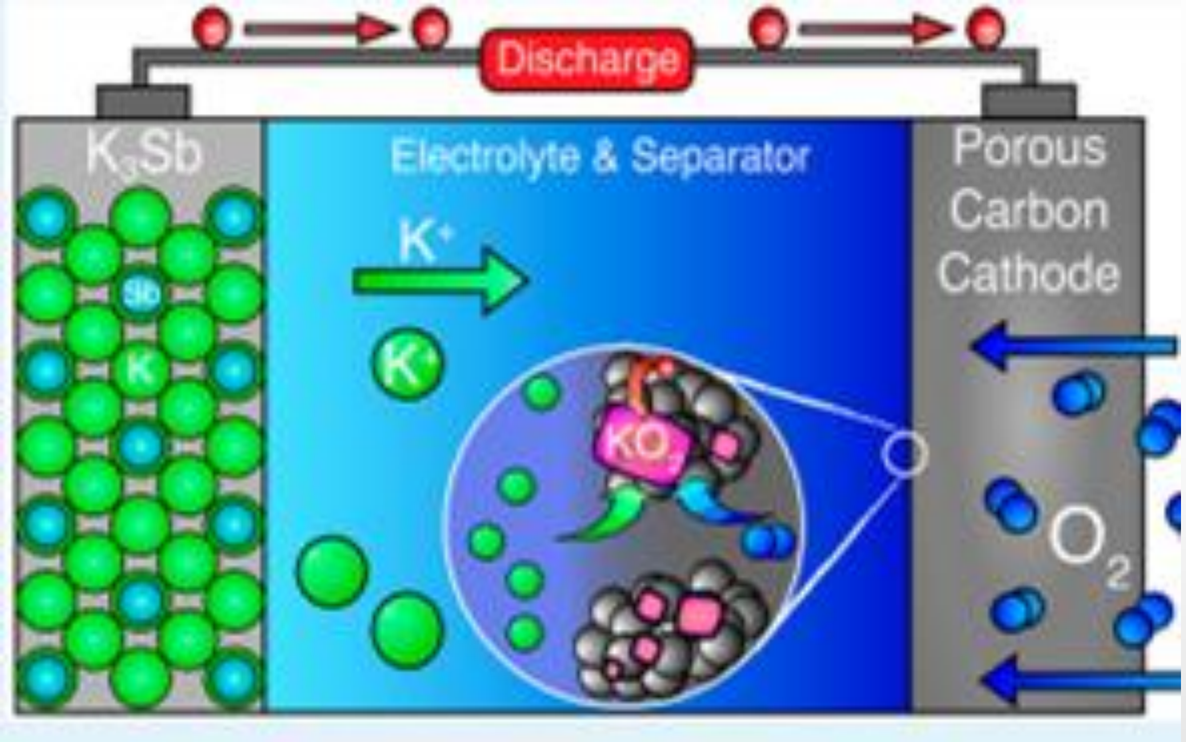


Accessed (11/17/2016)
https://www.google.com/search?q=Industry&espv=2&biw=1600&bih=721&source=lnms&tbm=isch&sa=X&ved=0ahUKEwjInOqQkrHQAhUDeSYKHUBYCF4Q_AUICCgD#imgrc=_gGSgq7grxFscM%3A
https://www.google.com/search?q=corrosion&espv=2&biw=1600&bih=721&site=webhp&source=lnms&tbm=isch&sa=X&ved=0ahUKEwi5w4S5p7HQAhXGRCYKHYNDAmUQ_AUIBygC#imgrc=dlpgxVUFqVTrzM%3A

K_3Sb Alloy

- Semiconductors in the solid state.
- Cubic phase
- Liquid alloys change continuously from metallic to nonmetallic

K_3Sb in Oxygen Batteries



$$K_3Sb \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} 3K^+ + 3e^- + Sb$$

$$O_2 + e^- + K^+ \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} KO_2$$

*McCulloch, W.D et. al. Potassium-Ion Oxygen Battery Based on a High Capacity Antimony Anode. Appl. Mater. Interfaces. 7, 26158 26166, (**2015**).*

Conclusions of this application

- Potassium can reversibly alloy with antimony
- They form a cubic phase K_3Sb with a high capacity of 650 mAh/g.
- Sb as a powerful electrode because the low cost of ~$10/kg and high theoretical capacity.

Antimony: Biological properties

15/VA

51

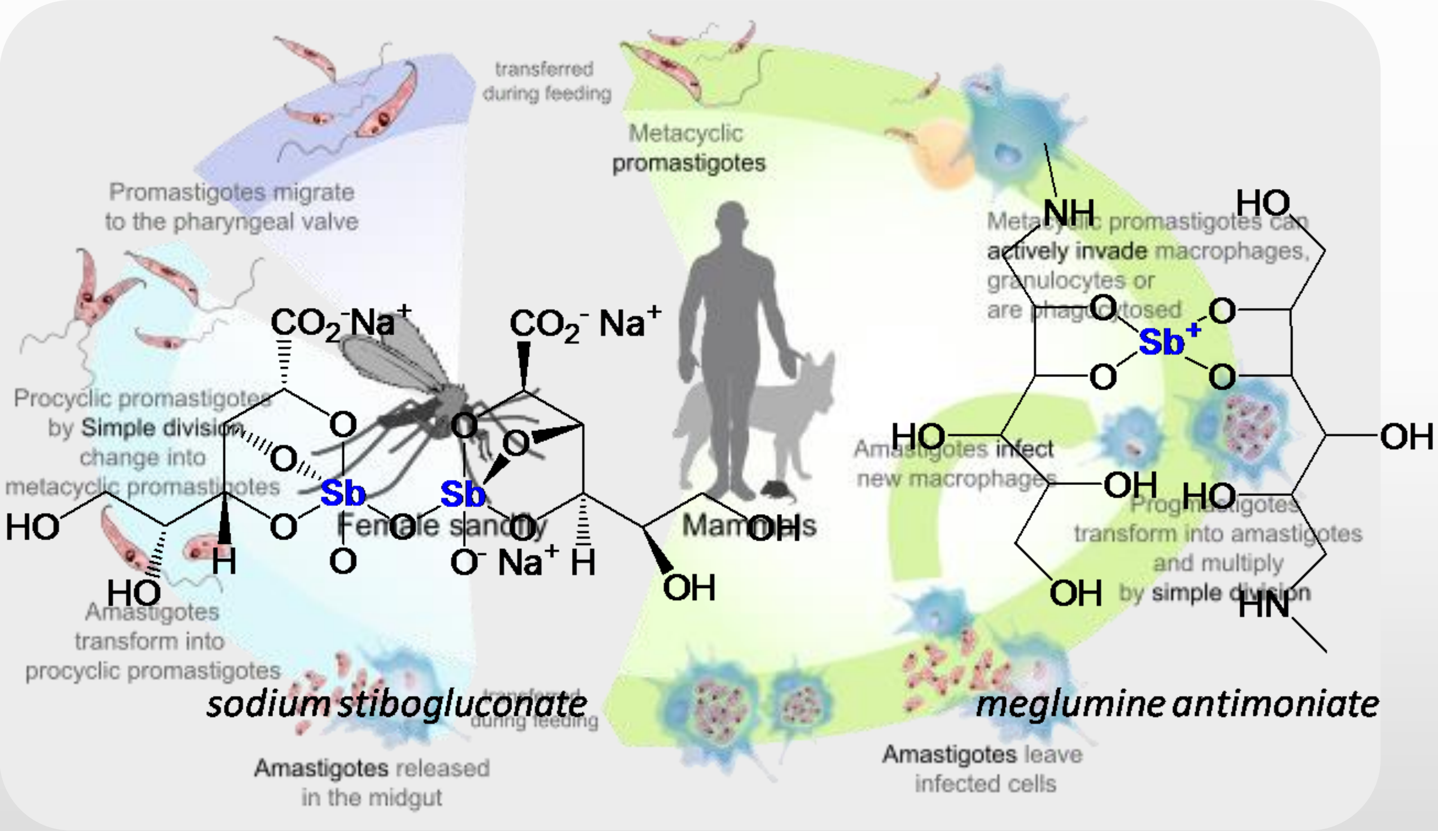
121,75

+3,5

Sb

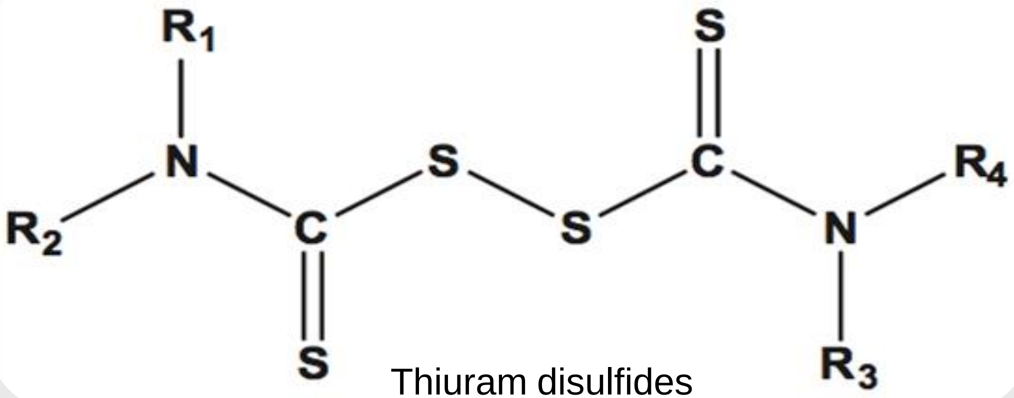
$5s^2 5p^3$

Sb(V): Anti-protozoal

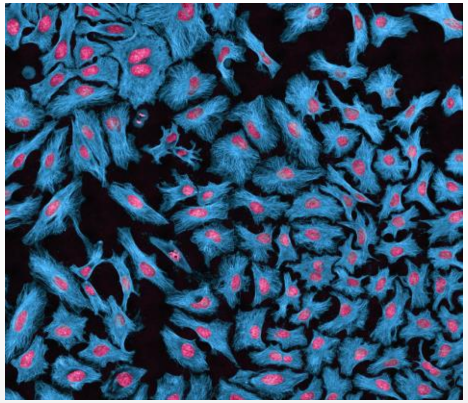


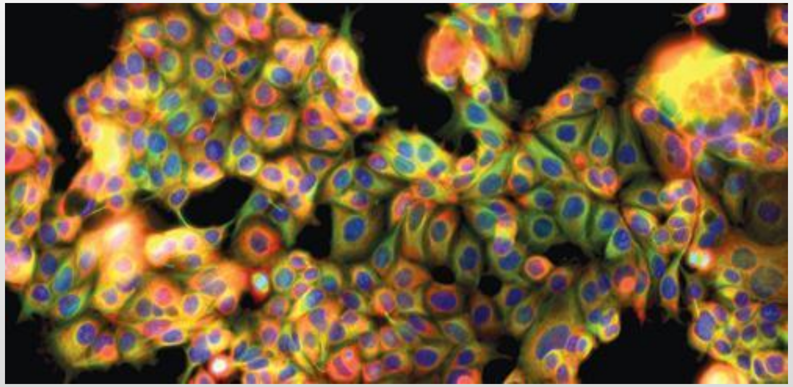
https://en.wikipedia.org/wiki/Leishmaniasis#/media/File:Leishmaniasis_life_cycle_diagram_en.svg
https://en.wikipedia.org/wiki/Leishmaniasis#/media/File:Skin_ulcer_due_to_leishmaniasis,_hand_of_Central_American_adult_3MG0037_lores.jpg
http://www.intechopen.com/books/leishmaniasis-trends-in-epidemiology-diagnosis-and-treatment/metal-based-therapeutics-for-leishmaniasis

Sb(III): Anti-cancer



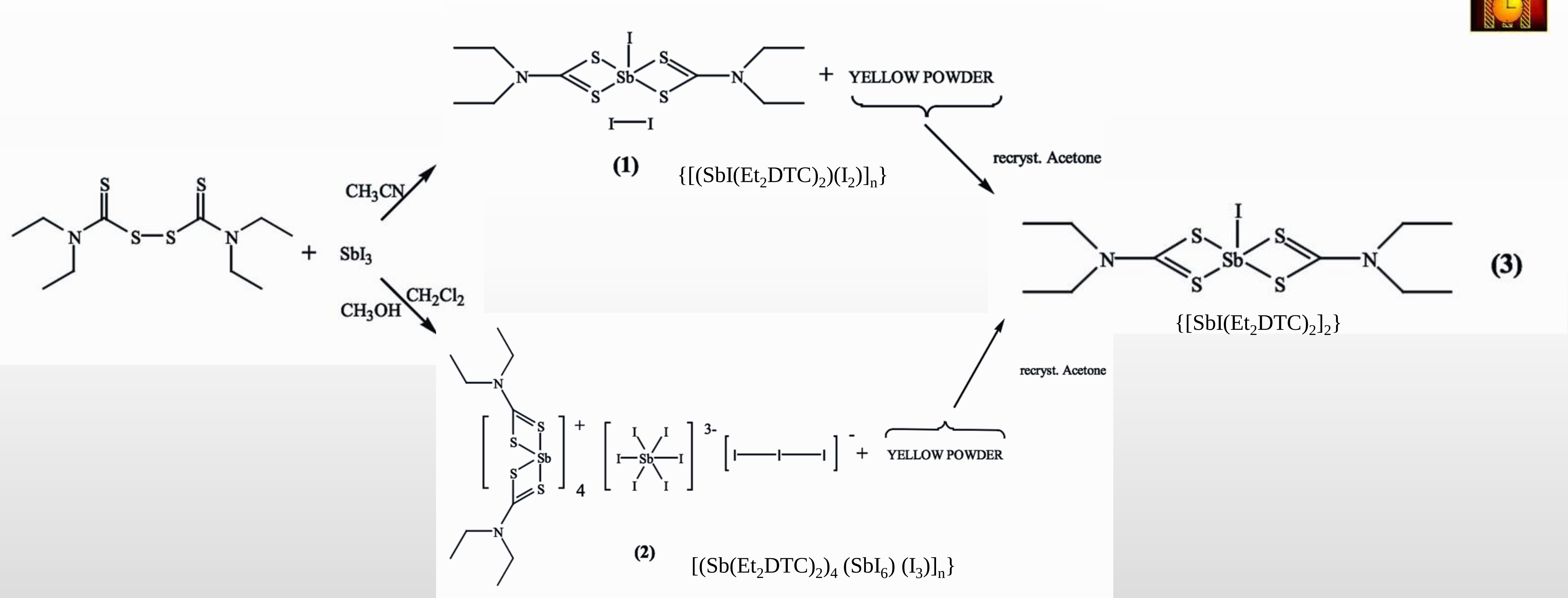
Thiuram disulfides





Urgut, O.S., Ozturk, I.I., Banti, C.N., Kourkoumelis, N., Manoli, M., Tasiopoulos, A.J. & Hadjikakou, S.K. Addition of tetraethylthiuram disulfide to antimony(III) iodide; synthesis, characterization and biological activity. *Inor. Chim. Act.* **443**, 141-150 (2016).

Antimony as anticancer drug



Urgut, O.S., Ozturk, I.I., Banti, C.N., Kourkoumelis, N., Manoli, M., Tasiopoulos, A.J. & Hadjikakou, S.K. Addition of tetraethylthiuram disulfide to antimony(III) iodide; synthesis, characterization and biological activity. *Inor. Chim. Act.* **443**, 141-150 (2016).

^{1}H-NMR Characterization

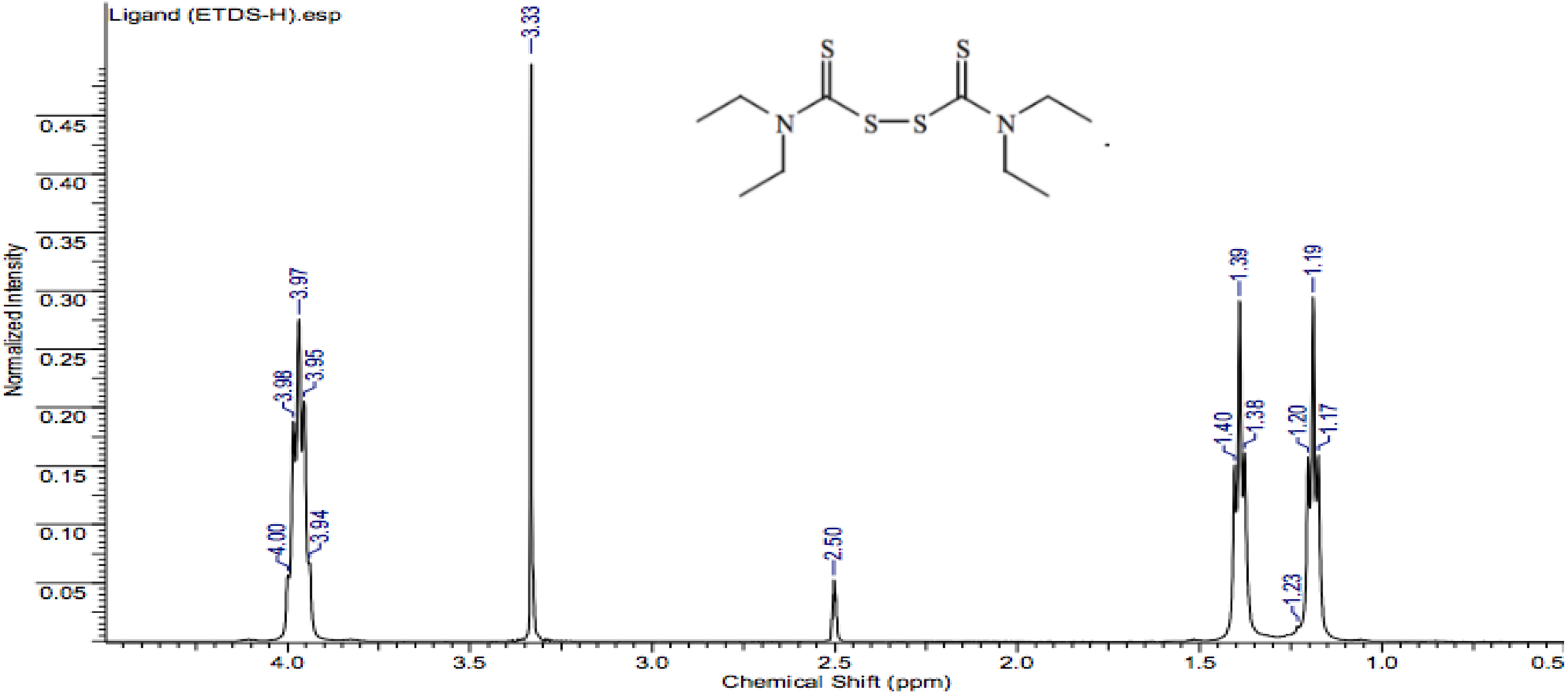


Figure S14 ^{1}H-NMR spectrum of the ligand

Urgut, O.S., Ozturk, I.I., Banti, C.N., Kourkoumelis, N., Manoli, M., Tasiopoulos, A.J. & Hadjikakou, S.K. Addition of tetraethylthiuram disulfide to antimony(III) iodide; synthesis, characterization and biological activity. *Inor. Chim. Act.* **443**, 141-150 (2016).

^{1}H-NMR Characterization

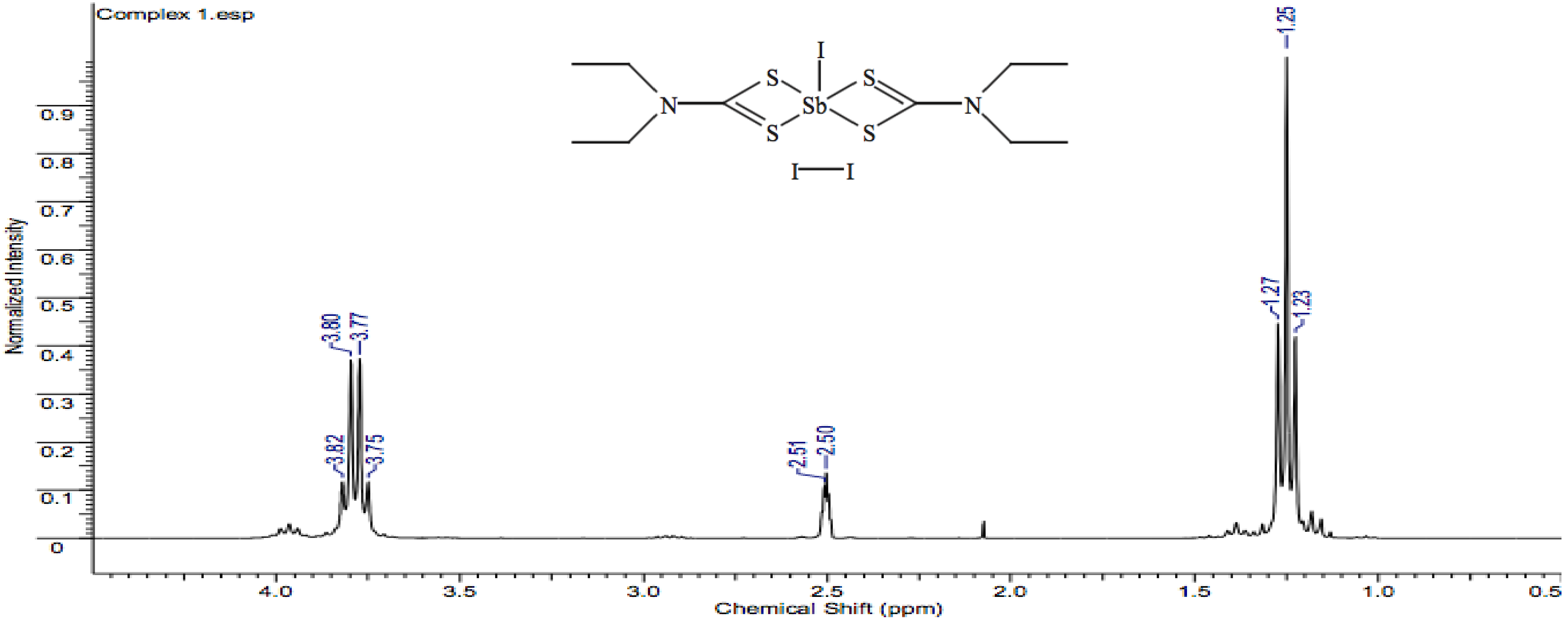


Figure S11. ^{1}H-NMR spectrum of **1**

Urgut, O.S., Ozturk, I.I., Banti, C.N., Kourkoumelis, N., Manoli, M., Tasiopoulos, A.J. & Hadjikakou, S.K. Addition of tetraethylthiuram disulfide to antimony(III) iodide; synthesis, characterization and biological activity. *Inor. Chim. Act.* **443**, 141-150 (2016).

^{1}H-NMR Characterization

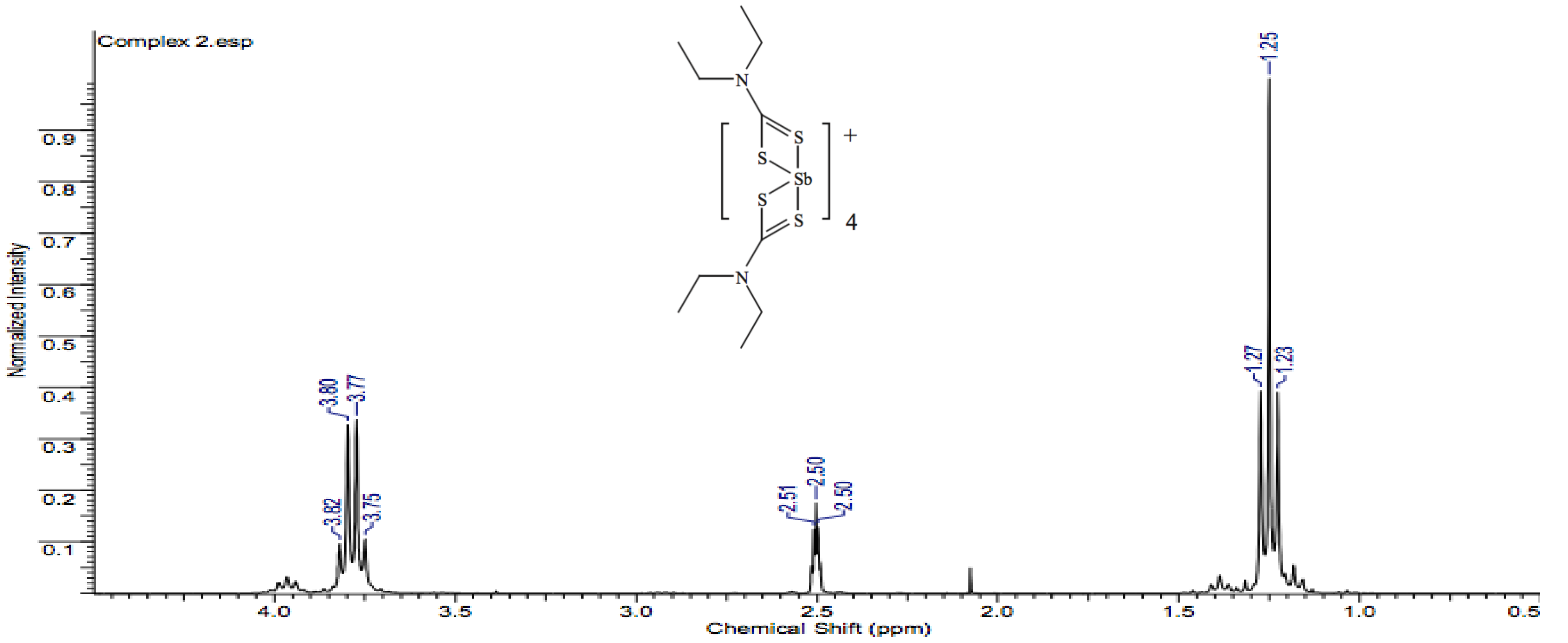


Figure S12. ^{1}H-NMR spectrum of **2**

Urgut, O.S., Ozturk, I.I., Banti, C.N., Kourkoumelis, N., Manoli, M., Tasiopoulos, A.J. & Hadjikakou, S.K. Addition of tetraethylthiuram disulfide to antimony(III) iodide; synthesis, characterization and biological activity. *Inor. Chim. Act.* **443**, 141-150 (2016).

^{1}H-NMR Characterization

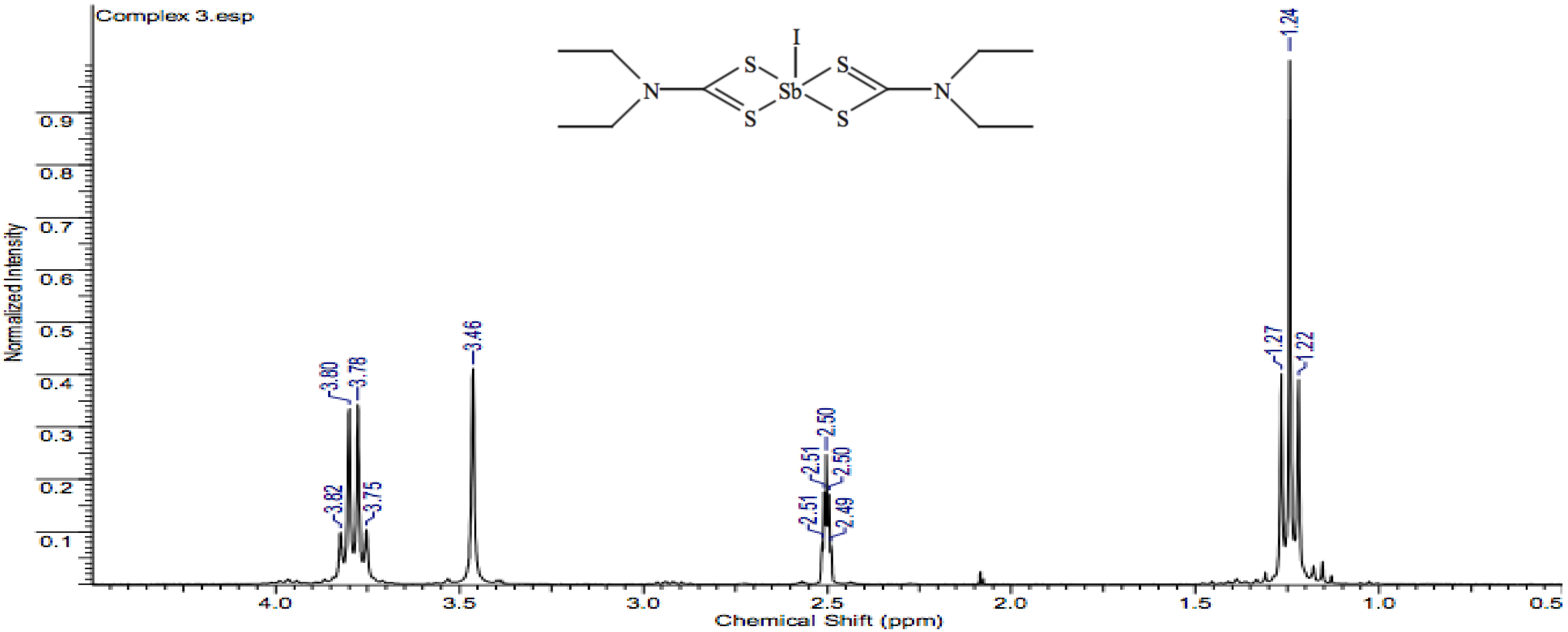


Figure S13 ^{1}H-NMR spectrum of 3

Urgut, O.S., Ozturk, I.I., Banti, C.N., Kourkoumelis, N., Manoli, M., Tasiopoulos, A.J. & Hadjikakou, S.K. Addition of tetraethylthiuram disulfide to antimony(III) iodide; synthesis, characterization and biological activity. *Inor. Chim. Act.* **443**, 141-150 (2016).

Cell biological assay

IC_{50} values for cell viability found for complexes **1–3** and other complexes Sb(III) against HeLa (cervix), MCF-7 (breast).

Complexes	Volume (A^3)	Contacts[a](%)	IC_{50} (μM)	
			HeLa	MCF-7
$\{[(SbI(Et_2DTC)_2)(I_2)]_n\}$ (**1**),	552.3	70.3	0.07 ± 0.007	0.04 ± 0.002
$\{[(Sb(Et_2DTC)_2)_4\ (SbI_6)\ (I_3)]_n\}$ (**2**)	1229.2	68.1	0.75 ± 0.04	0.5 ± 0.04
$\{[SbI(Et_2DTC)_2]_2\}$ (**3**)	431.7	74.4	1.8 ± 0.2	0.05 ± 0.005
$\{[SbI(Me_2DTC)_2]_n\}$ (**4**)	338.78	66.1	0.037 ± 0.001	0.047 ± 0.003
$\{[(Me_2DTC)_2Sb(\mu_2\text{-}I)Sb(Me_2DTC)_2]^+ \cdot I_3^-\}$ (**5**)	795.43	61.2	0.023 ± 0.001	0.019 ± 0.002
$\{[SbBr(Me_2DTC)_2]_n\}$ (**6**)	330.08	66.7	0.046 ± 0.004	0.09 ± 0.003
$\{[SbCl(Me_2DTC)_2]_n\}$ (**7**)	330.6	65.2	0.46 ± 0.07	0.02 ± 0.003
$\{[SbCl(Me_2DTC)_2]_n\}$(**8**)	331.19	66.5	0.51 ± 0.10	0.024 ± 0.004
$\{[SbI_3(HDTOA)_{1.5}] \cdot C_6H_6\}_n$ **(9)**	1327.48	78.2	11.82 ± 1.10	18.42 ± 1.41
$\{[SbBr_3(HDTOA)_{1.5}]\}_n$ **(10)**	1376.07	79	8.49 ± 0.65	21.64 ± 1.89
$\{[SbCl_3(HDTOA)_{1.5}]\}_n$ **(11)**	1375.44	78.6	–	12.4 ± 1.56
$\{[(SbI_2(\mu_2\text{-}I)(Hthcl)_2)_2]\}$ **(12)**	1044.64	74.8	–	0.76 ± 0.16
$\{[(SbBr_2(\mu_2\text{-}Br)(Hthcl)_2)_2]\}$ **(13)**	974.73	76.6	–	1.44 ± 0.36
$\{[SbCl_2(\mu_2\text{-}Cl)(Hthcl)_2]_n\}$ **(14)**	498.77	70.1	–	12.23 ± 2.27
$\{[SbBr_2(DETU)_2]^+Br^-\}_n$ (**15**)	493.92	78.8	12.4 ± 2.1	17.6 ± 1.7
$\{[mer\text{-}SbCl_3(DIPTU)_3][fac\text{-}SbCl_3(DIPTU)_3]\ C_6H_6\}$ (**16**)	458.93	84	7.7 ± 1.3	13.2 ± 1.2
Cisplatin			10	6.8

Urgut, O.S., Ozturk, I.I., Banti, C.N., Kourkoumelis, N., Manoli, M., Tasiopoulos, A.J. & Hadjikakou, S.K. Addition of tetraethylthiuram disulfide to antimony(III) iodide; synthesis, characterization and biological activity. *Inor. Chim. Act.* **443**, 141-150 (2016).

Conclusions

- Sb(III) and Sb(V) has anti-protozoal and anti-cancer properties.
- Sb(V) induce the parasite dies by apoptosis.
- Complex of Sb(III) demonstrate greater potency.
- IC_{50} confirm the potency of Sb(III) complex.

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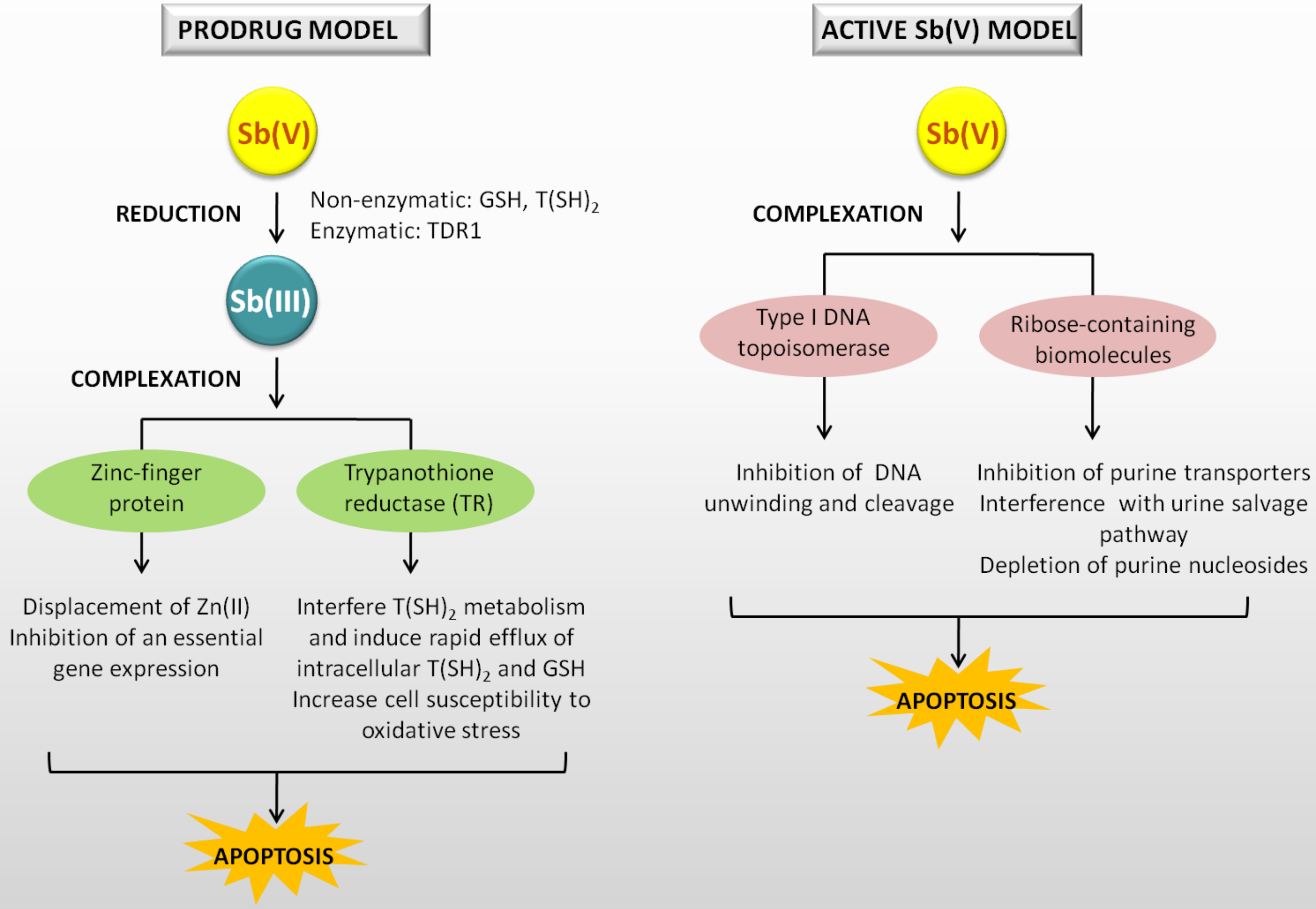
Thank you for your attention!

QUESTIONS??

Mechanism


PRODRUG MODEL
Sb(V)
REDUCTION
Non-enzymatic: GSH, T(SH)2
Enzymatic: TDR1
Sb(III)
COMPLEXATION
Zinc-finger protein
Trypanothione reductase (TR)
Displacement of Zn(II)
Inhibition of an essential gene expression
Interfere T(SH)2 metabolism and induce rapid efflux of intracellular T(SH)2 and GSH
Increase cell susceptibility to oxidative stress
APOPTOSIS
ACTIVE Sb(V) MODEL
Sb(V)
COMPLEXATION
Type I DNA topoisomerase
Ribose-containing biomolecules
Inhibition of DNA unwinding and cleavage
Inhibition of purine transporters
Interference with urine salvage pathway
Depletion of purine nucleosides
APOPTOSIS