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Synthesis And Characterization Of Some New Organotellurium - Dithiocarbamate Complexes

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ABSTRACT

Tellurium with thiourea-derived bonds in the formula ($RNHCS_2^-$ or $R_2NCS_2^-$) is a stable complex with yellow color and foul odor, characterized and analyzed by FT-IR, HNMR, and mass spectrometry. The percentage of elements included in the sample composition was known by EDX, EDS technique, and the surface topography was studied using a by Field Emission Scanning Electron Microscopy FSEM.

Keywords: Tellurium, Organotellurium, Dithiocarbamates , Diphenylthiourea

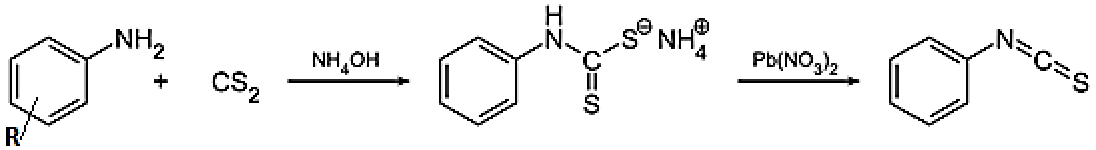
1.1. INTRODUCTION

Dithiocarbamate group ($RNHCS_2^-$ or $R2NCS_2^-$) tend to form stable complexes with most elements of the periodic table d-block [1,2,3,4] ore p-block metal ions [5,6,7]. It is a chelating ligand with a soft base that is one of the most effective, The principle of hard and soft Acide Bases [8] is used to bend powerfully with Tellurium (IV) .Tellurium(IV) dithiocarbamate complexes are used for a various Applications,such as anti-tuberculosis agents[9], catalysts for use in the rubber vulcanization accelerators[10,11].

They are also used in polypropylene as stabilizers [5 ,10] . Though thiourea and its derivatives generally reduce Te (IV) in acid solution into stable divalent telluriume compelexes, stable compelexes of tetravalent tellurium have also been isolated [12,13]. In this paper, we present the synthesis of new tellurium(IV)-dithiocarbamate complexes by reaction of some thiourea derivatives prepared by Blended aniline with carbon disulfide[15] and investigate their properties and composition . The new Tellurium(IV)-dithiocarbamate structures used in this paper are shown in Figure 1.

Experimental & Materials

All of the materials and solvents used in this work were analytical reagent grade from Sigma Aldrich or British Drug House . and were used exactly as directed. All the glassware used in the preparation was thoroughly washed with tap water and a soap solution then rinsed with acetone with distilled water before drying in the oven. After the materials are carefully processed, the experiment is set up in the fume cupboard with a magnetic stirrer, magnetic bar stirrer, reaction vessel, and a clean dried Erlenmeyer flask. Compounds (I-X I) in the table were prepared according to [15].



R= H, CH3 , X , OH , Ph , Benzyl ,NO_2, ...

Preparation of N,N-Diphenylthiourea

The compound was prepare by mixing 5 ml of aniline with 10 ml of carbon disulfide, 25% ammonium hydroxide solution, and lead monoxide (5 g pbO dissolved in 25 ml ethanol) Refulx 4hrs then filter the solution to get (black sediment neglected), and the yellow filtrate was preserved in Petri dish to get attractive golden needle crystals of N,N-Diphenylthiourea. The compounds (II- IX) were prepared by reacting the Diphenyl Thiourea Derivatives with Tellurium dioxide dissolved in ethanol with Refulx for about 90 minutes at Room temperature. The products were purified by recrystallization and Thin Layer Chromatography TLC and verified by their melting points and IR spectra.

Physical measurements

The IR spectra were recorded in the range 4000-400cm^{-1} on a Shimadzu spectrometer using KBr discs . ^{1}H NMR spectra were measured on a Bruker DRX 500 MHz (Germany) at 400MHz with TMS as an internal reference. DMSO d6 as solvent used . Microanalyses for carbon, hydrogen, sulfur, nitrogen ,oxygen and Tellerium were carried out on energy dispersive X-ray analysis (EDXA or EDAX) , the Characterization morphological surface by Field emission scanning electron microscopy (FESEM) . All characterization results was recorded at Central Laboratory,College of Science,Tahran university and Central Laboratory of Sherif Sanaaty university, Islamic Republic of Iran except IR spectra It was recognized at Department of Chemistry- faculty of science- Basrah University. At Tarbiat Modares University/ iran, mass spectra of some of the prepared compounds were recorded using Agilent Technologies EI at an electronic energy of 70 electron volts.

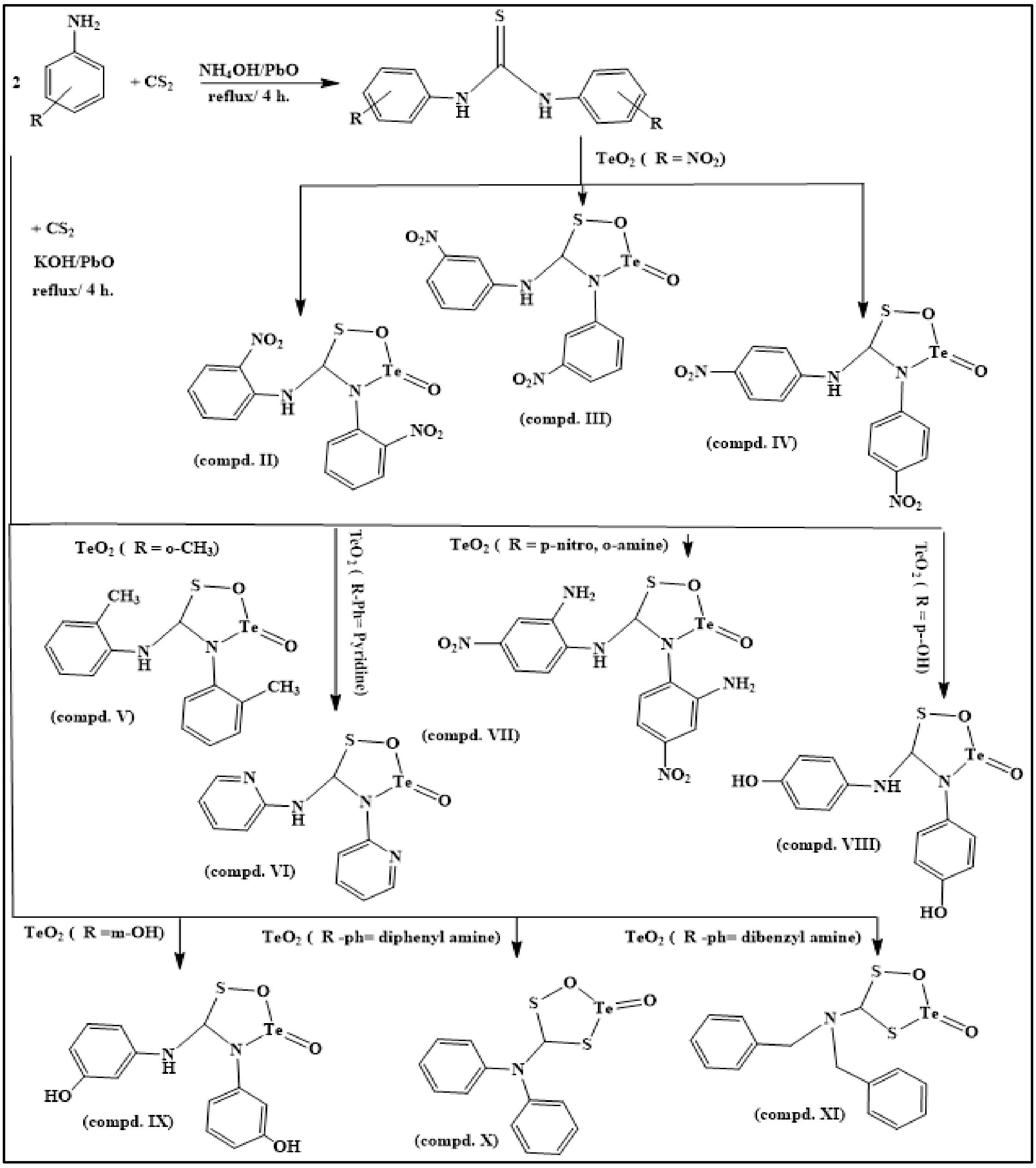


Figure 1 . The scheme for expected chemical structures of the prepared compounds

RESULTS AND DISCUSSION

The ligand N,N-Diphenylthiourea was prepared as light yellow in good yield. Isolated yields, melting points and analytical data for the newly synthesized complexes (I-XI) are listed in Table.1. All the new compounds are pale yellow solids and highly soluble in solvents such as Petroleum Ether, Benzene, Tetrahydrofuran(THF) and Chloroform but are less soluble in Methanol and Ethanol. although this solubility becomes lower than that of the precursors from which the compounds were prepared after tellurium linked due to the disappearance of hydrogen bonds. When matching the ligand and complex IR spectra, the disappearance band 3171 cm^{-1} was ascribed to the υ (N-H) of the ligand [16], confirming the interaction of tellurium with the nitrogen atom. Where it was observed that there are two band (3171 cm^{-1} , 3452cm^{-1}) for compound I , We haven't seen it on other complexes . There was a strong and sharp band at 2000 cm^{-1} with each compounds back to C-S except for compound I where appear with its band 748cm^{-1} belongs to C=S. Table 2. ^{1}HNMR data fot the complexes I-XI , at the estimated chemical shift , all aromatic protons were observed at (6.5-7.5 ppm) , in agreement with literature data show [17]. The downfield chemical shifts of 8.6 ppm are characteristic of the tow NH groups, while the chemical shifts at about (6.5 – 6.8 ppm) Returns to the part of the amine group attached to the organic part of the telleuride , this resulted in to agree with other work[18].

Table 1: Melting points , UV-Vis. and IR Data New prepared Tellurium dithiocarbamate.

Com No.	MP (^{o}C)	UV- Visible Spectra			Infrared Spectra for main bands(cm^{-1})						
		Band I	Band II	Band III	C=C	C-H Ar ,st	C-H ale	C-S [16]	N-H [19]	Te-N [20]	Te=O [21]
I	120	252	206	-	1654	3071	2943	-	3448	-	-
II	89	396	244	204	1597	3101	3016	2060	3483	524	663
III	70	401	254	209	1627	3132	3015	2060	3448	550	682
IV	78	372	227	204	1631	3101	3010	2060	3479	532	628
V	90	363	221	200	1618	3165	3024	2065	3425	540	667
VI	97	333	260	204	1627	3100	2982	2065	3436	500	667
VII	125	304	266	206	1653	3101	3070	2060	3448	553	617
VIII	146	400	253	207	1618	3165	3024	2065	3425	555	640
IX	145	353	221	202	1618	3165	3024	2065	3425	555	640
X	120	384	227	208	1625	2980	2933	2060	3448	555	670
XI	142	378	217	206	1647	3100	3010	2060	3448	536	678

Ar , Aromatic .st, stretching . ale, alefatic

Ultaviolet Visible uv-vis Specroscopy

ultaviolet visible (uv-vis) Specroscopy for compounds are recorded from (200-800 nm). It showed three absorption bands attributable to the π-$\pi*$ and n-$\pi*$ transitions[4,22]. This is to be expected, as the prepared compounds have yellow and orange colours .

Table (2). H -NMR spectral data for the complexes I-XI.

Com No.	**^{1}H NMR spectra (ppm) DMSO-d6 solvent .TMS = 0ppm**
I	8.6 (NH ,s, H1,H14) ;6.5- 7.4 (Ar-H, , H3 – H12) ; 5.6 (CH)
II	6.8 (NH,s,1H) ; 7.06- 7.58, (H4, H5, H6, H14, H15, H16 ; 5.9- H25), 8-8.1(H3 , H13)
III	6.6 (NH,s,1H) ; 7.06- 7.78, (H3, H5, H6, H15, H16, H18 H20), 8. (H5) ; 5.7(H20)
IV	6.1 (NH,s,1H) ; 7.02- 7.5, (H4,H5, H6, H10, H11) ; 2.3 (CH3 , H17,H18)
V	7.2 (NH,s,1H) ; 6.9 - 7.31 (m) ph- protons ; 2.5 DMSO
VI	6.5 (NH,s,1H) ; 7.09- 7.9, (H3,H5, H6, H14, H16, H17) ; 5.2 (NH2 , H11,H21) ; 5.7 CH , H23
VII	6.5 (NH,s,1H) ; 6.5- 7.9, (H2,H3,H5, H6, H11, H12, H14,H15) ; 8.9 (OH , H7,H10) ; 5.7 CH , H17
VIII ,IX	6.6 (NH,s,1H) ; 6.5- 7.5, (H2,H3,H7, H10, H12, H13, H14) ; 8.5 (OH , H0,H20) ; 5.8 CH , H15
X	1.06 (NH,s,1H) ; NH (7.3) ; 7.05- 7.5 (Ph-H , 20H) ; 3.8 (CH-Te)
XI	7- 7.5, (H-,H5,H8- H12, H16- H20, H23-H27)

Analysis of elemental composition of synthesized compounds by EDX & EDS.
Analysis of Energy Dispersive X-ray specroscopy EDX , EDS ore EDXAS anylasis conected with scaning Elecrone micoscope SEM , were used to anylsis Elementes comisition and chemical characterization of compounds . EDX spectra of synthesized compounds as shown in the Figures below In which is indicated the wight percentage of the elements in the composition of the compounds , The proportion of tellurium in compound (I) is zero because the ligand has not yet bonded with it, while in other compounds it appears in a different percentage . The appearance of the peaks at energy Kev starts with the element with the lowest atomic mass, which is carbon, and ends with the most atomic mass, which is tellurium. The height of the peak depends on the ratio of the element in the compound .The peak of the gold belongs to the material from which the model holder is made in theinstrumental of the scanning electron microscope.

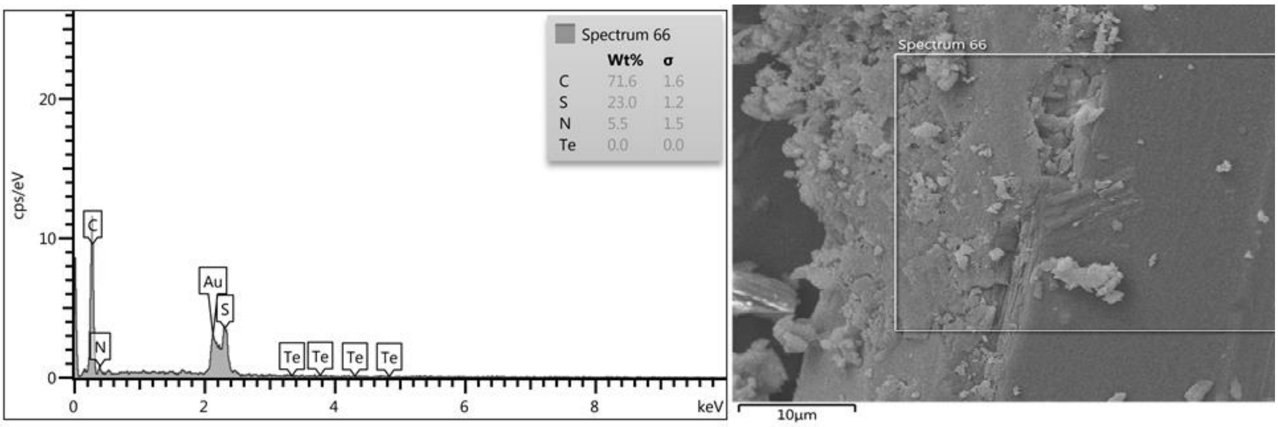


Figure 1: Shows EDX spectra whight Elemental percentage of different elements in compund.(I) (C:71.6% , S:23%,N:5.5 , Te:0)

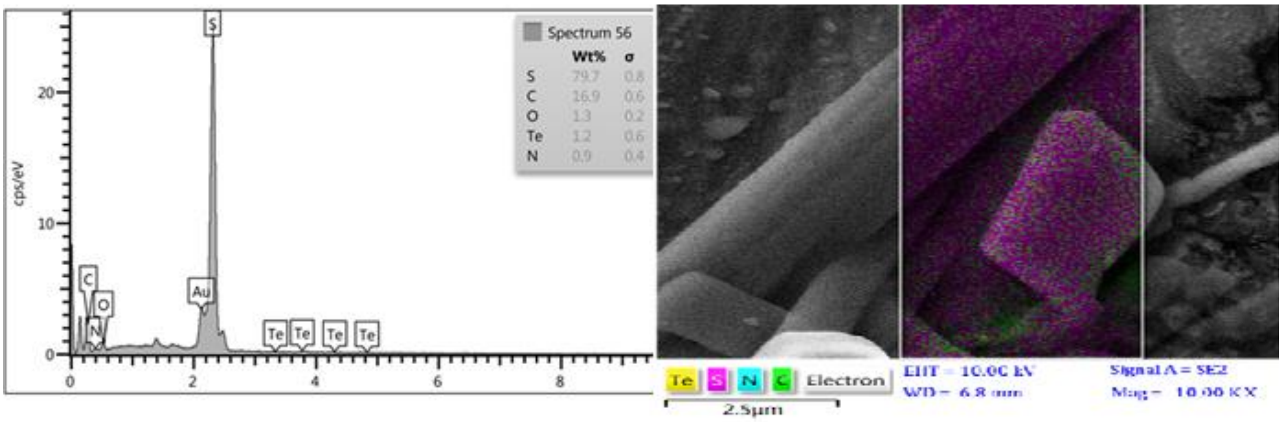


Figure 2: Shows EDX spectra whight Elemental percentage of different elements in compund.(II) (C:79.7% , 16:6%,N:0.9% , Te:1.2%, O:1.35%). EDAX, each element appears in color .

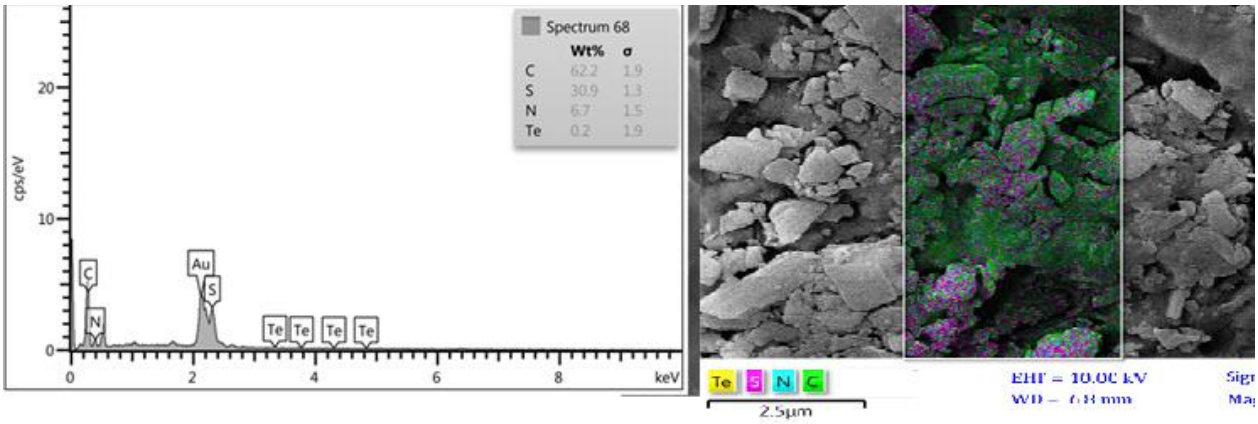


Figure 3: Shows EDX spectra whight Elemental percentage of different elements in compund.(III) (C:62.2% , S:30:9%,N:6.7% , Te:0.2%,). EDAX, each element appears in color .

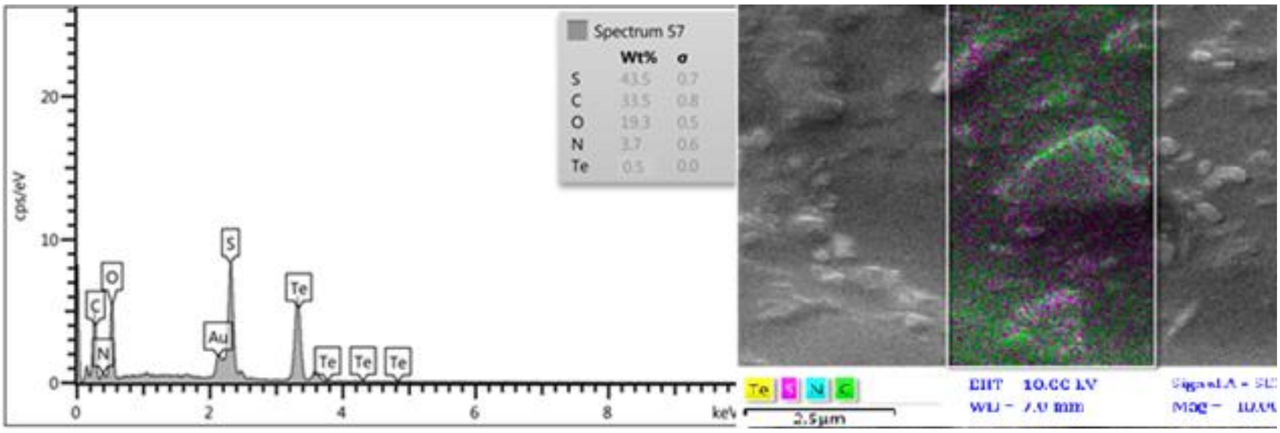


Figure 4: Shows EDX spectra whight Elemental percentage of different elements in compund.(V) (C:33.5% ,S 43:5%,N:3.7% , Te:0.5 %, O:19.3%). EDAX, each element appears in color .

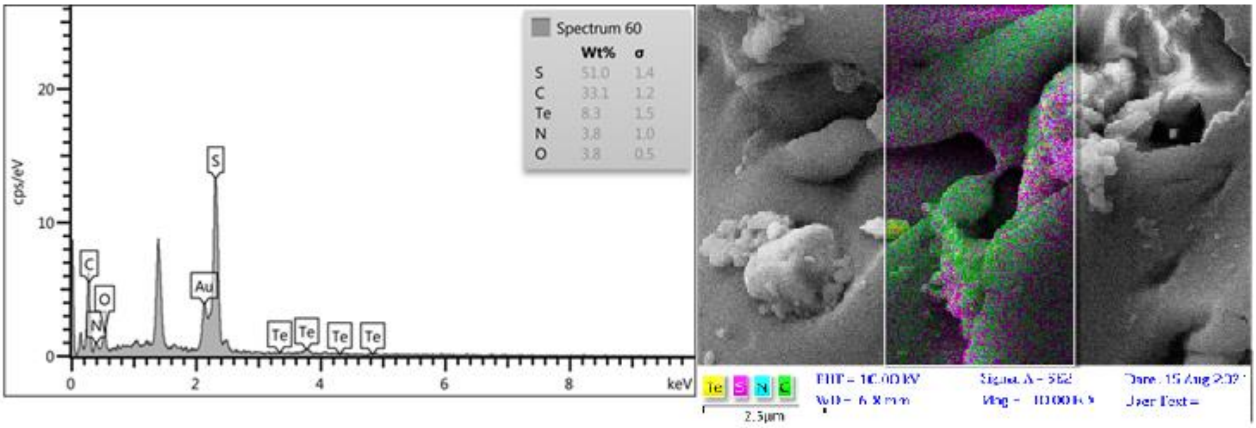


Figure 5: Shows EDX spectra whight Elemental percentage of different elements in compund.(VIII) (C:33. % ,S 51%,N:3.8% , Te:8.3%, O:3.8%). EDAX, each element appears in color .

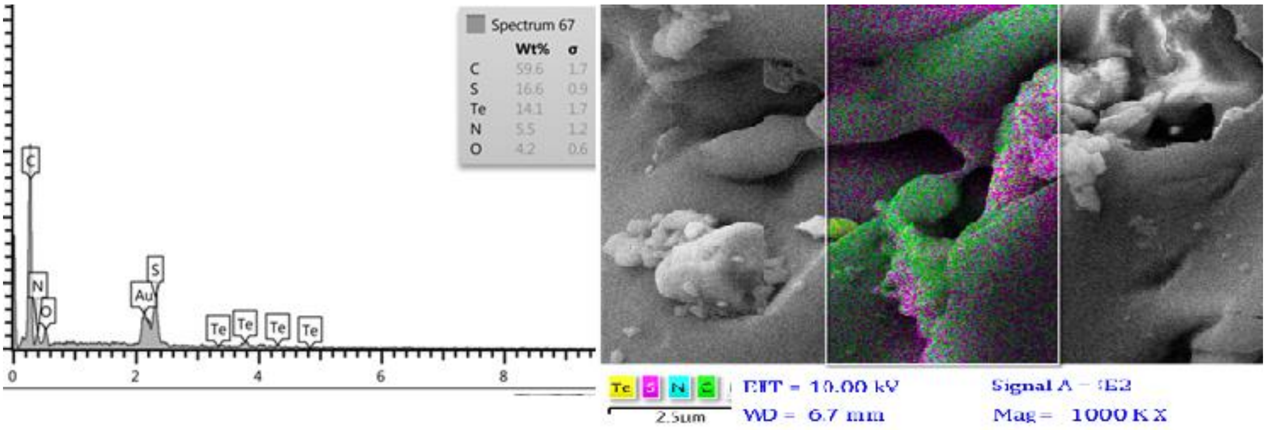


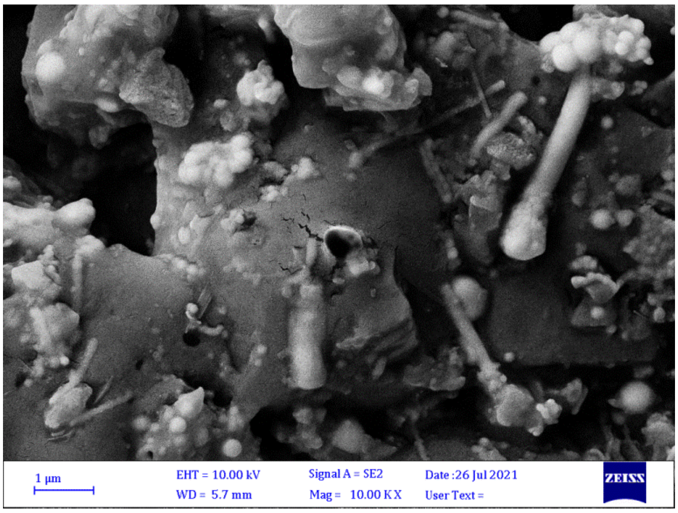
Figure 6: Shows EDX spectra whight Elemental percentage of different elements in compund.(II) (C:59.6% ,S: 16:6%,N:5.5% , Te:14.1%, O:0.6%). EDAX, each element appears in color .

Mass Spectrometry

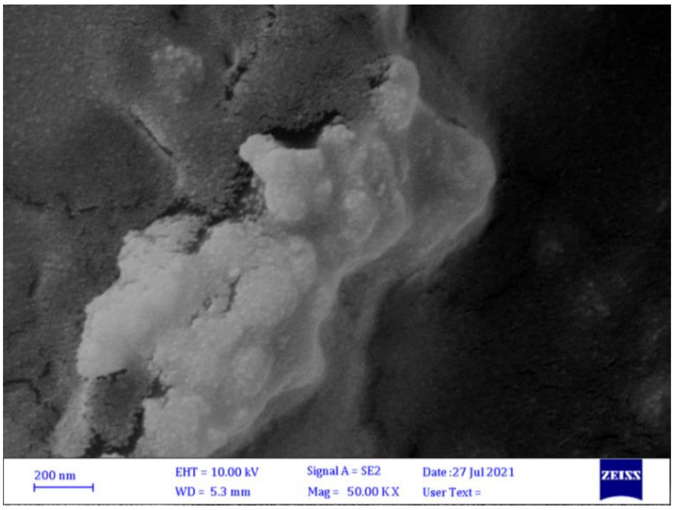
At 70 eV, Mass SpectrometryMS was used to investigate compounds The fragmentation of the compounds is noticeable in the mass spectra. The absence of a molecular ion may be related to dissociation occurs below 70eV [19]. MS of compound I shows a peak at m/z 59 which is corresponding to $[CHNS]^+$ and appearance of a peak at m/z 93 belonging to the base ion to $[C_6H_6N]^+$,high relative abundance at m/z to$[C_7H_7N_2]^+$. for compounds (II ,III ,IV) MS specra shows a peak at m/z 477.91 which is corresponding to $[C_{13}H_{10}N_4STe]^{2+}$ and appearance of a peak at m/z 59 belonging to the base ion to $[CHNO_2]^{2+}$. High relative abundance at m/z 92 to $2[NO_2]^+$ and High relative abundance m/z at 138 associated with $[C_6H_5N_2O_2]^+$ also High relative abundance at m/z = 159 for $[NOTe]^+$. for compound (V), the MS specra shows a peak at m/z 415 which is corresponding to $[C_{13}H_{10}N_4STe]^{2+}$ and appearance of a peak at m/z 59 and 93 belonging to the base ion to $[CH2NS]^{2+}$, $[C_7H_7]^+$ respectively. High relative abundance at m/z 195 to $[O_2Te]^{+2}$ and High relative abundance m/z at 255.8 associated with $[C_4H_3NO_2S\ Te]^{4+}$ also High relative abundance at m/z = 332 for $[C_8H_9N_2O_2S\ Te]^+$. The compound VI has molecular mass 389g/mol, High relative abundance at m/z = 44 ,77 belonging to the base ion to $[OS]^+$, $[C_5H_4N]^+$ respectively. m/z=106 , $[C_6H_6N_2]^+$, m/z= $[C_6H_6N_3]^+$, m/z=236 $[CH_2N_2OSTe\ ]^+$, m/z= $[C_6H_6N_3O_2STe]^+$.The compound VII has molecular mass 509g/mol, High relative abundance at m/z = 209 belonging to the base ion to $[CHO_2STe]^{2+}$,m/z=44 , $[CHS]^+$, m/z=163 $[O_2Te]^+$, m/z=255 $[C_{12}H1_2N_2O_2\ ]^+$. The compoundes VII, IX have molecular mass 421 g/mol, High relative abundance at m/z = 93belonging to the base ion to $[C_6H_5O]^+$,m/z=60, $[C_4H_4O]^+$. The compound X has molecular mass 630 g/mol, High relative abundance at m/z =91 belonging to the base ion to $[C_6H_5N]^+$, m/z=193.7 , $[O_2STe]^+$, m/z=255.8 $[C_{14}H_{13}N_3S]^{2+}$. Compound XI his relative abundance m/z = 600.11 $[C_{29}H_{30}N_2O_2STe]^{2+}$, m/z =91 $[C_7H_7]^+$, m/z =119$[C_8H_9N]^+$.

Characterization morphological surface by FESEM of synthesized compounds .

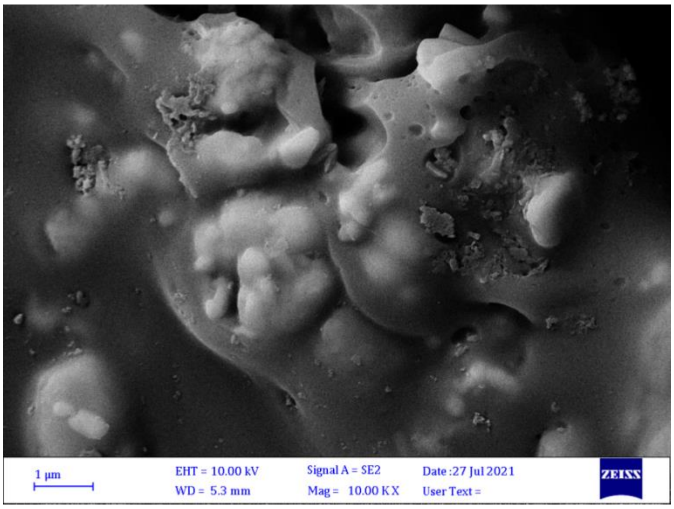
Field Emission Scanning Electron Microscopy (FESEM) technical analysis is used to examine the properties morphological surface of the prepared compounds [23]. The images below are a selection of images taken by shining an electron beam accelerating at a voltage of 15kV onto the sample surface through a Field Emission scanning electron microscope gun, By employing electromagnetic lenses with magnification range 20X- 5000X , images of different depths were obtained from the surface of the samples by used FEI NOVA nanosem450, instrumental in Tehran University.



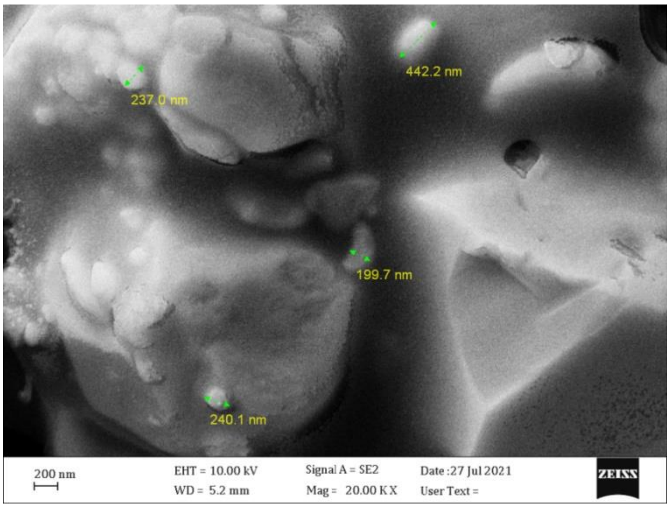
FSEM spectrum of compound.(I)



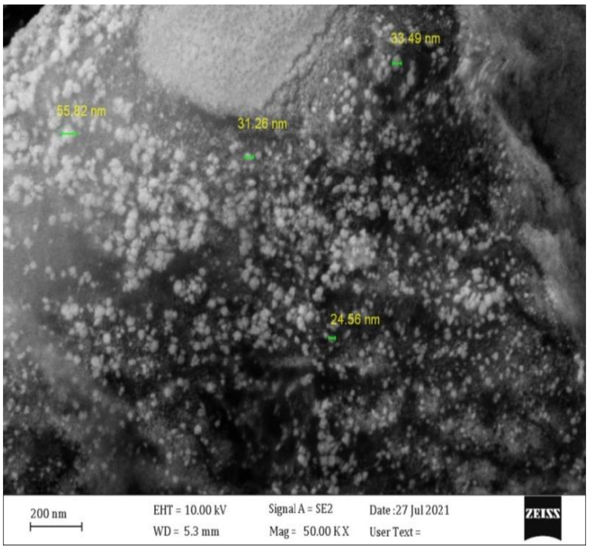
FSEM spectrum of compound.(II)



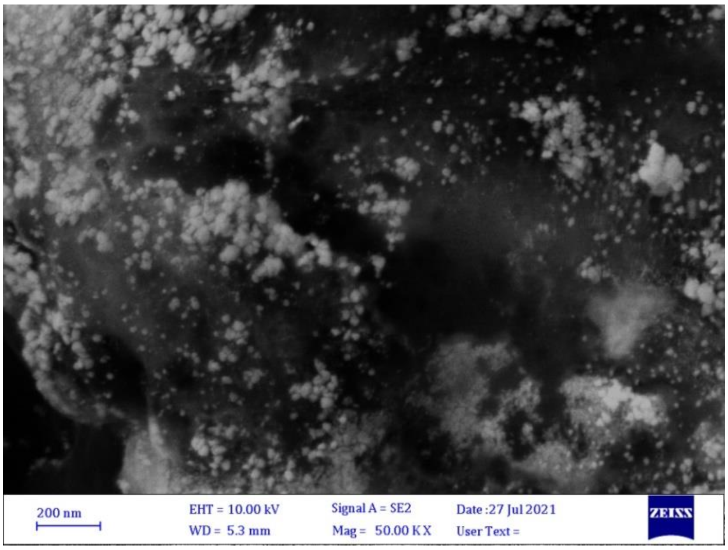
FSEM spectrum of compound.(III)



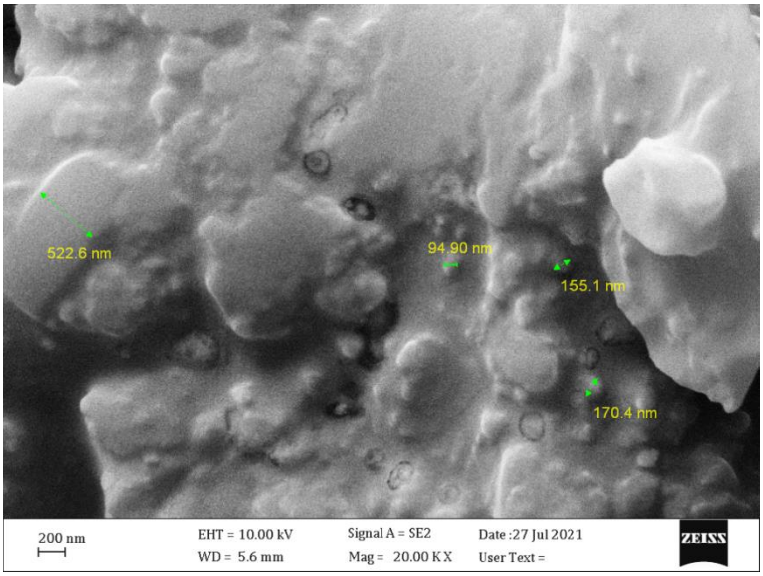
FSEM spectrum of compound.(V)



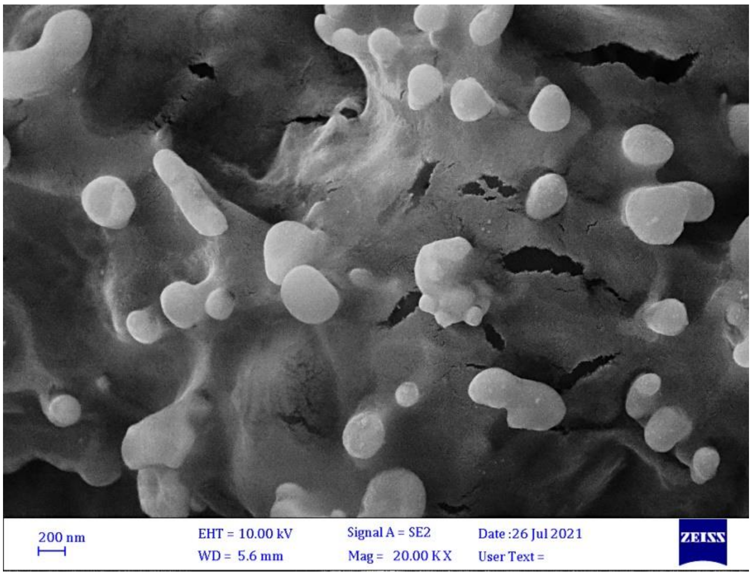
FSEM spectrum of compound.(VI)



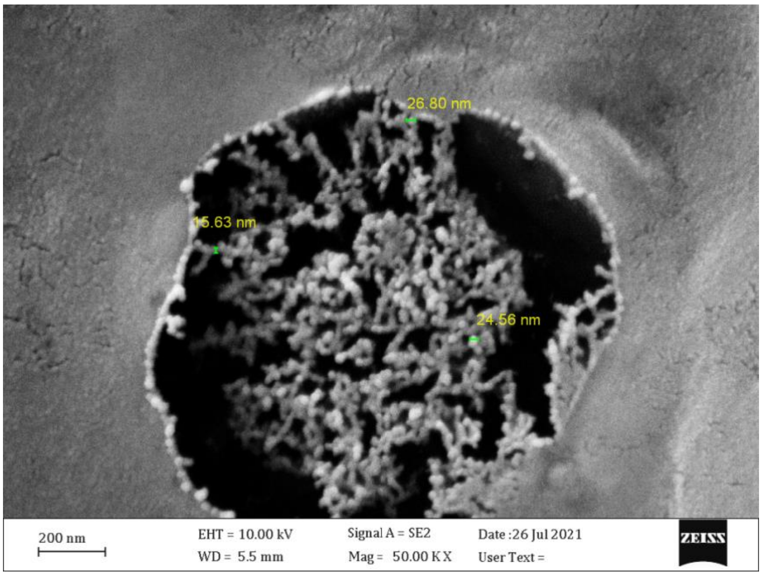
FSEM spectrum of comp.(VII)



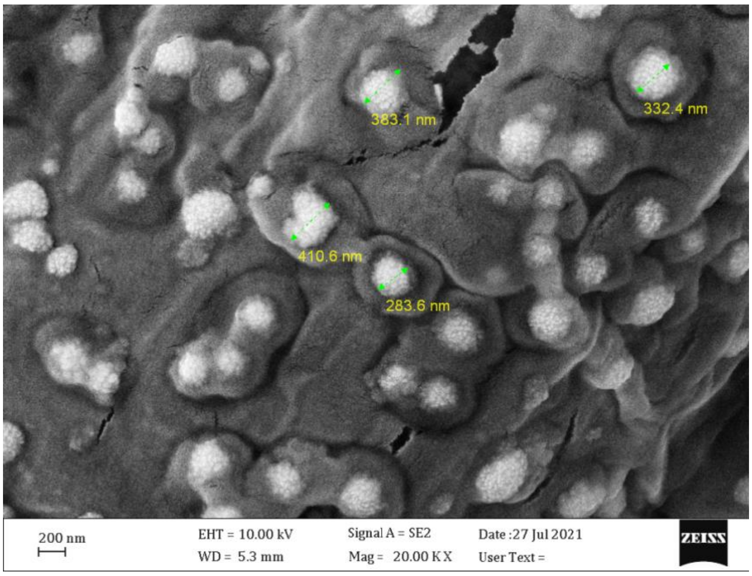
FSEM spectrum of compound.(VIII)



FSEM spectrum of compound.(IX)



FSEM spectrum of comp.(X)



FSEM spectrum of comp.(XI)

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