Synthesis, characterization and antioxidant measurements of selenium (IV) complexes with some amino acids - binuclear complexes


INTRODUCTION

Generally, amino acids containing two essential groups (amine and carboxylic acid) attached to the first α-carbon atom, are of particular importance in biochemical field. The chemical formula of α-amino acids is H₂NCHRCOOH in most cases where, R is an organic substituent known as a side-chain [1, 2]. Amino acids are the main structural chemical constituents of proteins, which enter into the structure of all living organisms and are the most important factor in biochemical processes that support the preservation of human life [3, 4]. They are highly susceptible to being excellent catalysts and can be chelated with transition metals through their amino or carboxylic groups [5, 6]. Over the past few decades the complexion of transitional metal ions with amino acids has been studied [7, 8].

The amino acid reactions were found to be responsible for the enzymatic activity and stability of protein structures [9, 10]. The complexity of mineral amino acids is an important area of research where they can be used as simulated systems to identify the interaction of mineral protein in biological systems.

Selenium is one of the rarer elements present in low and fundamental concentrations in the human body and is of great importance in nutrition and medicine [11]. Selenium nanoparticles have some unique optical, mechanical, electrical, biological and chemical properties as compared to other chemicals. For example, selenium nanoparticles have been reported to have high biological activity and low toxicity [12], and nanowires of selenium with trigonal geometry have new optical photoconductivity [13]. Thus, selenium...
nanoparticles attracted considerable interest of researchers and different synthesis methods were exploited [14-17].

Amino acid coordination chemistry is an integral feature of inorganic and bioinorganic chemistry [18-20], with many applications in medicinal design and materials science [21, 22]. Selenium amino acid complexes attract attention of chemists because of their different kinds of applications. In selenium (IV) amino acid complexes syntheses, the amino acid is first reacted with a selenium (IV) ion and gives stable octahedral selenium (IV) complexes. In this paper an overview on structures and coordination chemistry of selenium (IV) amino acid complexes is given. This article describes the synthesis of selenium nanoparticles by in situ amino acid chelation. This study presents preliminary results of synthesized bis-chelated complexes of the used five amino acids, shown in Fig. 1.

![Chemical structures of the used five amino acids](image)

**Fig. 1:** Chemical structures of the used five amino acids

**MATERIALS AND METHODS**

**Chemicals and reagents**

The amino acids (L-configuration) asparagine (Asn), proline (Pro), glutamine (Gln), methionine (Met) and cysteine (Cys) were purchased from Sigma-Aldrich Chemical Company, all organic solvents and reagents were used in pure form. SeCl₄ was received from Aldrich Company.

**Synthesis of selenium (IV) amino acid complexes**

The collected compounds were prepared using the same chemical procedures, as follows: adding 25 mL of amino acids in ethanol (4 mmol) to the same volume of selenium (IV) tetrachloride also in ethanol (2 mmol). The solutions were refluxed for 2 h and the resultant brown to black-brown solution was reduced to ca. 1/2 of its volume. The solids produced by filtration were collected and washed with petroleum ether (60-80°C) and dried in a vacuum medium over anhydrous CaCl₂.

**Instruments**

- Elemental analysis (%C, %H and %N) percentage was performed using Perkin Elmer CHN 2400.
- Molar conductivity (10⁻³ mol/cm³) with dimethylsulfoxide (DMSO) solvent was determined using Jenway 4010 conductivity meter.
- Electronic spectra were scanned using UV-3101 PC Shimadzu spectrophotometer.
- FT-IR spectra were scanned on a Bruker FT-IR spectrophotometer.
- Raman laser spectra were collected on a Bruker FT-Raman spectrophotometer equipped with a 50 mW.
- ¹H-NMR spectra were recorded using a Varian Gemini 200 MHz spectrometer.
- Mass spectra were scanned using AEI MS 30 mass spectrometer with 70 eV.
- Thermal study TG/DTG–50H was carried out on a Shimadzu thermogravimetric analyzer under nitrogen atmosphere.
- Scanning electron microscopy (SEM) was performed on Quanta FEG 250 equipment.
- X-ray powder diffraction was measured on XPert PRO PANanalytical with target Cu with secondary monochromator.

**DPPH and Hydroxyl Radical Scavenging assays**

The 2, 2-diphenyl-1-picrylhydrazyl (DPPH) assay was performed as described in [23]. Free radical damage imposed on the substrate, deoxyribose, was measured using the thiobarbituric acid test [24, 25]. The inhibition (I) percentage of deoxyribose degradation was experimentally calculated using the following relationship:

\[ I(\%) = 100 \times \left( \frac{A_0 - A_1}{A_0} \right) \]

where \(A_0\) is the absorbance of the control sample and \(A_1\) is the absorbance of the tested sample. Statistical analysis: each of the measurements described was conducted in at least three identical trials and the results were reported as mean and standard deviation, significantly different calculated level at \(p \leq 0.05\).

**RESULTS AND DISCUSSION**

**Microanalysis results**

Analytical results for the synthesized selenium (IV) amino acid complexes are listed in Table 1.
Table 1: Elemental analysis and physical data of \([\text{Se}^{4+}(\text{AA}^{-1})_2\text{Cl}_2]\) complexes

<table>
<thead>
<tr>
<th>Complex/Complex</th>
<th>Empirical formula</th>
<th>M. wt. g/mole</th>
<th>% C</th>
<th>% H</th>
<th>% N</th>
<th>Mp/°C</th>
<th>Color</th>
<th>Λm (Ω(^{-1}) cm(^2) mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Se(Asn)}_2\text{Cl}_2]) I</td>
<td>(\text{C}<em>8\text{H}</em>{14}\text{Cl}_2\text{N}_4\text{O}_6\text{Se, I})</td>
<td>412.09</td>
<td>(23.32)</td>
<td>(3.42)</td>
<td>(13.60)</td>
<td>179</td>
<td>Brown</td>
<td>27</td>
</tr>
<tr>
<td>([\text{Se(Pro)}_2\text{Cl}_2]) II</td>
<td>(\text{C}<em>{10}\text{H}</em>{16}\text{Cl}_2\text{N}_2\text{O}_4\text{Se, II})</td>
<td>378.11</td>
<td>(31.77)</td>
<td>(4.27)</td>
<td>(7.41)</td>
<td>185</td>
<td>Brown</td>
<td>25</td>
</tr>
<tr>
<td>([\text{Se(Gln)}_2\text{Cl}_2]) III</td>
<td>(\text{C}<em>{10}\text{H}</em>{18}\text{Cl}_2\text{N}_4\text{O}_6\text{Se, III})</td>
<td>440.14</td>
<td>(27.29)</td>
<td>(4.12)</td>
<td>(12.73)</td>
<td>210</td>
<td>Red brown</td>
<td>43</td>
</tr>
<tr>
<td>([\text{Se(Met)}_2\text{Cl}_2]) IV</td>
<td>(\text{C}<em>{10}\text{H}</em>{20}\text{Cl}_2\text{N}_2\text{O}_4\text{S}_2\text{Se, IV})</td>
<td>446.27</td>
<td>(26.91)</td>
<td>(4.52)</td>
<td>(6.28)</td>
<td>201</td>
<td>Red brown</td>
<td>32</td>
</tr>
<tr>
<td>([\text{Se(Cys)}_2\text{Cl}_2]) V</td>
<td>(\text{C}<em>6\text{H}</em>{12}\text{Cl}_2\text{N}_2\text{O}_4\text{S}_2\text{Se, V})</td>
<td>390.17</td>
<td>(18.47)</td>
<td>(3.10)</td>
<td>(7.18)</td>
<td>245</td>
<td>Black brown</td>
<td>38</td>
</tr>
</tbody>
</table>

These support the formation of binuclear complexes with chemical composition of 1:2 selenium to amino acid stoichiometry. All complexes are colored, and soluble in DMF and DMSO. The elemental analysis in Table 1 matched well with 1:2 (Se: amino acid) ratio. For selenium complexes, the molar conductivities are in the range of 25-43 ohm\(^{-1}\) cm\(^2\) mol\(^{-1}\). These values deduced that 1:2 complexes are non-electrolytes soluble in DMSO [26, 27]. These results are regarded to be low due to the existence of the two chlorine atoms inside the coordination sphere. These complexes have a melting point within the 179-245 °C range, with yield of 80-88%. The presence of \(\text{Cl}^-\) ions was checked using AgNO\(_3\) reagent.

Electronic spectra

The shift of \(n-\pi^*\) characteristic band in the UV-Vis spectra, attributed to the C=O bond (272 nm for Asn-Se, 272 nm for Pro-Se, 276 nm for Gln-Se, 294 nm for Met-Se and 264 nm for Cys-Se) is due to the involving of the non-bonding electron pairs of the oxygen in the metal-ligand bond formation, Fig. 2. The formation of amino acids SeNPs was confirmed with the help of UV–Vis spectra investigation according to the change in color from colorless (selenium(IV) chloride) to three degrees of brown color (SeNPs), having absorption maximum \(\lambda_{\text{max}}\) at 300–400 nm [28].

Infrared spectra

FT-IR spectra of the five investigated complexes are illustrated in Figs. 3a-e. These spectra display very similar spectral bands, so the coordination behavior in all selenium (IV) complexes I-V is similar. The proposed spectral assignments are presented in Table 2.
In the spectrum of selenium (IV)-Cys complex, the infrared frequencies at 1622 and 1407 cm\(^{-1}\) were assigned to antisymmetric and symmetric COO\(^-\) frequencies, respectively. In free Cys the SH frequency appears at 2548 cm\(^{-1}\) but the infrared spectrum of Se(IV)–Cys complex shows no SH absorption frequency. The absence of SH frequency in the spectrum of the complex is an evidence of the involvement of S group in complexation with metal. The NH\(_2\) frequencies are found to be at 3027, 1487 and 1125 cm\(^{-1}\). Antisymmetric and symmetric COO\(^-\) frequencies in Se-Asn, Se-Pro, Se-Gln and Se-Met complexes are at (1667 and 1403) cm\(^{-1}\), (1621 and 1403) cm\(^{-1}\), (1593 and 1402) cm\(^{-1}\), and (1617 and 1409) cm\(^{-1}\), respectively. There are no NH\(_2\) bending frequencies in the spectra of these complexes as expected from the symmetry consideration. The complexes exhibit two new frequencies at 600-500 and 500-400 cm\(^{-1}\), respectively, due to Se-O and Se-N stretching [33]. The Se-Gln complex has medium string band at 1682 cm\(^{-1}\) attributed to stretching vibration of the carbonyl of the amido group. From IR data, the energy difference between both \(\nu_{as}(\text{COO}^{-})\) and \(\nu_{s}(\text{COO}^{-})\) vibrations (\(\Delta = 191-264\) cm\(^{-1}\)) clearly supports the participation of carboxylate group in monodentate binding [34].

**Proton Magnetic Resonance Spectra**

The chemical shifts of Se-Cys (V) complex are shown in Fig. 6. The spectrum of complex V possesses two characteristic signals. The sharp signal due to the –CH and –CH2 proton is observed around 3.31 ppm. The singlet broad signal of the –NH\(_3\) protons is located at 7.01 ppm. The resonance due to the proton of the –OH and –SH groups (11-12 ppm) of the Cys chelate disappears in the selenium (IV) complex (V) indicating that coordination has taken place through the deprotonation of –OH and binding of S atom of –SH.
Finally, the presence of a singlet broad band at 7.01 ppm is due to the faraway of nitrogen atom of –NH$_2$ from complexation, Fig. 4.

**Table 2.** IR frequencies (cm$^{-1}$) of [Se(AA)$_2$Cl$_2$] complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\nu$(O-H)</th>
<th>$\nu$(N-H)</th>
<th>$\nu$(COO$^-$)</th>
<th>$\delta$(NH$_2$)</th>
<th>$\nu$(M-O)</th>
<th>$\nu$(M-N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>3163</td>
<td>1667</td>
<td>1403</td>
<td>--</td>
<td>524</td>
<td>466</td>
</tr>
<tr>
<td>II</td>
<td>3136</td>
<td>1621</td>
<td>1403</td>
<td>--</td>
<td>520</td>
<td>470</td>
</tr>
<tr>
<td>III</td>
<td>3180</td>
<td>1593</td>
<td>1402</td>
<td>--</td>
<td>497</td>
<td>428</td>
</tr>
<tr>
<td>IV</td>
<td>3124</td>
<td>1617</td>
<td>1409</td>
<td>--</td>
<td>523</td>
<td>439</td>
</tr>
<tr>
<td>V</td>
<td>3027</td>
<td>1622</td>
<td>1407</td>
<td>1487</td>
<td>540</td>
<td>455</td>
</tr>
</tbody>
</table>

**Fig. 4.** Speculated structures of [Se(AA)$_2$Cl$_2$] complexes (AA= Asp, Pro, Glu, Met and Cys).

**Fig. 5.** Raman laser spectrum of a- Se-Met and b- Se-Cys complexes.
Mass Spectra

Chemical shifts of the Se-Cys (V) complex: The mass spectral data of the [Se(Cys)$_2$(Cl)$_2$] complex are presented in Fig. 7. The mass spectrum of Se-Cys complex showed a molecular ion peak that is in a good agreement with the expected value. The mass spectrum of Se-Cys shows a peak at 390 m/z, which was assigned as a [M] peak. The Cys molecule was thought to produce ions at m/z 345, 329, 284,252, 219,200, 168, 135, 105, 64, and 63, respectively. The m/z 78 ion, which is a Se-Cys (V) complex, is containing one selenium atom.

XRD Spectra

The X-ray diffraction patterns of the [Se(Cys)$_2$(Cl)$_2$] complex with selenium nanoparticles are shown in Fig. 8. The diffraction peaks present at 2θ (degrees) of 23.42°, 29.57°, 42.05°, 43.75°, 45.47°, 51.43°, 55.70°, 61.46°, 65.09° and 71.59° correspond to (100), (101), (110), (102), (111), (201), (112), (202), (210) and (113) planes of selenium, respectively. The diffraction peaks within the 2θ region due to hexagonal crystal structure of selenium are in agreement with the standard data (JCPDS card No. 01-071-4647), as shown in Fig. 9. The particle size of selenium was estimated using Scherrer’s eq. [36]

$$D = \frac{0.9λ}{β\cosθ}$$

where D = grain size, K = constant equal to 0.94, λ = wavelength of the X-ray radiation, β = full width at half maximum and θ = diffraction angle. The particle size of selenium nanoparticles is found to
be ~ 10 nm. The diffraction pattern due to (100), (101), (110), (102), (111) and (201) directions of hexagonal phase of selenium is shown in Fig. 9.

![Fig. 8. XRD spectrum of Se-Cys complex.](image)

The d-spacing values for the diffraction pattern match well with the hexagonal selenium.

![Fig. 9. Standard XRD spectrum of Cys and Se-Cys complex with selenium hexagonal structure.](image)
SEM, TEM and EDX Spectra

The scanning electron microscope (SEM) image of the [Se(\text{Cys})_2(\text{Cl})_2] complex with selenium nanorods and hexagonal structure is illustrated in Fig. 10. The SEM image reveals that the selenium nanorods are of uniform size with a mean diameter of ~10 nm. It can be seen that nanorods are of several micrometers in length with diameter ranging from 10 μm. Energy dispersive X-ray analysis (EDX) was used to identify and determine the chemical composition of the Se-Cys complex. EDX pattern of the Se-Cys complex is shown in Fig. 11. Weak signals concerning O atoms have been recorded along with the strong peak due to Se atom. EDX analysis indicates the presence of O, S, C, and Cl with very low intensity, so this analysis supported the purity of the selenium particles.

The transmission electron microscopy images were performed using JEOL 100s microscope. Fig. 12 shows the transmission electron microscope (TEM) image of Se-Cys complex selenium nanorods. The image shows that the nanorods are with an average diameter of ~10 nm.

Thermal analysis

Thermal stability of [Se(\text{AA})_2\text{Cl}_2] complexes (AA= Asn, Pro, Gin, Met and Cys) complexes was checked based on thermo gravimetric and its differential analyses started from room temperature till 800 °C under N₂ atmosphere. The TG curves were redrawn as mg mass loss versus temperature. The thermal decomposition curves (TG) are given in Fig. 13.

**Asn-Se complex**: Thermal decomposition of Asn-Se complex (I) occurs in four steps. The 1st degradation step takes place in the temperature range of 179-222 °C at DTG_{max} = 196 °C (endo) and it correspond to a mass loss of 15.043%. The 2nd step occur within the temperature range of 296-367 °C at DTG_{max} = 317 °C (endo) which was assigned to the decomposition of Asn molecule with a weight loss of 52.949%. The 3rd step occurs within the temperature range of 433-475 °C at DTG_{max} = 452
°C which is due to loss of organic moiety with a weight loss of 8.835%. The last decomposition step takes place within the temperature range of 573-663 °C with mass loss of 21.464%. The residual carbon atoms (1.709%) in the final product remain stable till 800 °C.

**Pro-Se complex:** The thermal decomposition of Pro-Se complex (II) occurs in three steps. The first degradation step takes place in the temperature range of 121-167 °C at DTG$_{max}$ = 136 °C (endo) and it corresponds to the loss of one chlorine atom with mass loss of 7.697%. The second step occurs within the temperature range of 275-383 °C at DTG$_{max}$ = 325 °C (endo) which was assigned to the decomposition of two Pro and one chlorine molecule with weight loss of 75.077%. The third step occurs within the temperature range of 527-625 °C at DTG$_{max}$ = 563 °C (endo) which was assigned to the loss of organic moiety with a weight loss of 12.420%. The few carbon atoms in the final product remain stable till 800 °C with mass loss of 4.806%.

**Gln-Se complex:** The thermal decomposition of Gln-Se complex (III) occurs in four successive steps. The first degradation step takes place in the temperature range of 46-55 °C at DTG$_{max}$ = 44 °C and it corresponds to the loss of water molecules with a weight loss of 2.183%. The second step occurs within the temperature range of 156-202 °C at DTG$_{max}$ = 172 °C (endo) which was assigned to the loss of one of the chlorine molecules beside the amino terminal groups with a weight loss of 10.069%. The third step occurs within the temperature range of 284-381 °C at DTG$_{max}$ = 328 °C (endo) which was assigned to the loss of organic moiety of Gln chelate with a weight loss of 54.740%. The fourth step occurs within the temperature range of 432-800 °C at DTG$_{max}$ = 500 °C which was assigned to the loss of organic moiety with a weight loss of 8.102%. The few carbon atoms with mass (24.906%) in the final product remain stable till 800 °C.

**Met-Se complex:** The thermal decomposition of Met-Se complex (IV) occurs in three steps. The first degradation step takes place in the temperature range of 128-146 °C at DTG$_{max}$ = 134 °C (endo) and it corresponds to the loss of chlorine atoms with a weight loss of 11.363%. The second step occurs within the temperature range of 257-303 °C at DTG$_{max}$ = 277 °C (endo) that was assigned to the loss of organic moiety with a weight loss of 56.139%. The third step occurs within the temperature range of 494-535 °C at DTG$_{max}$ = 511 °C that was assigned to the loss of organic moiety with a weight loss of 10.147%. The residual carbon with a mass of 2 2.351% in the final product remains stable till 800 °C.

**Cys-Se complex:** The thermal decomposition of Cys-Se complex (V) occurs in three successive steps. The first degradation step takes place in the temperature range of 265-305 °C at DTG$_{max}$ = 284 °C and it corresponds to the loss of two chlorine atoms and two molecules of Cys with weight loss of 70.559%. The second step occurs within the temperature range of 381-436 °C at DTG$_{max}$ = 397 °C which was assigned to the loss of organic moiety with a weight loss of 12.665%. The third step occurs within the temperature range of 448-558 °C at DTG$_{max}$ = 509 °C (endo) which was assigned to the loss of organic moiety with a weight loss of 11.700%. The residual few carbon atoms with m(VO$_2$ + C) in the final product remain stable till 800 °C as a final residue.

![Fig. 13. TG curves of [Se(AA)$_2$Cl$_2$] complexes (AA= Asn, Pro, Gln, Met and Cys).](image)

**Antioxidant activity**

Bioavailability of selenium from dietary supplements is strongly dependent on its chemical form. Seleno amino acids which possess organically bound selenium are considered to be better absorbed and less toxic than inorganic selenium compounds [37]. Many chemical materials have been evaluated for antioxidant activities using in vivo and in vitro models and the selenium compounds trial is one of the most successful. The aim of this work was to examine the antioxidant activities of five selenium amino acid complexes, DPPH and hydroxyl radical scavenging methods were applied to in vitro models. Resulted data indicated that the radical scavenging activities of the tested compounds depend on the chemical form of selenium. Radical scavenging activity effects of selenium complexes I-V against DPPH and hydroxyl radicals are shown...
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in Figs. 14 and 15. All concentrations (10, 20 and 30 ppm) of the tested complexes showed significant to moderate radical scavenging activity compared to standard BHA material (70.4, 85.1 and 94.3%), respectively. As shown in Figs. 14 and 15, the radical scavenging activity of all tested compounds gradually increases through all concentrations (10, 20 and 30 ppm) compared with butylated hydroxyanisole (BHA) as positive control.

Fig. 14. Diagrams of radical scavenging activity effects of selenium complexes I-V against DPPH.

Fig. 15. Diagrams of radical scavenging activity effects of selenium complexes I-V against hydroxyl radicals

The Se-Met and Se-Cys displayed the highest radical scavenging activity effects against DPPH compared with BHA. In the DPPH free radical scavenging test the stable yellow-colored diphenylpicrylhydrazine (DPPH-H) is formed in the presence of an antioxidant. The scavenging effects of BHA at concentrations 10, 20 and 30 ppm on the hydroxyl radical were 65.2, 78.3 and 86.5%, respectively. When the tested compounds or BHA were incubated with the reaction mixture they were able to interfere with free radical reaction and could prevent damage to the sugar.

CONCLUSION

Selenium(IV)-amino acids complexes of Asn, Pro, Gln, Met, and Cys were synthesized and characterized using analytical techniques such as elemental analysis, thermal analyses and (FT–IR, Raman laser, 1H-NMR, and UV–Vis) spectroscopy. The microanalytical elemental data deduced a 1:2 selenium ions: amino acid ratio of the synthesized complexes. In view of the FT-IR spectroscopy results the selenium (IV) ion was coordinated to the respective amino acids as a bidentate chelate. The geometry of the selenium ions was six-coordinated with those of amino acid complexes. The selenium in nano-structured form was investigated by Raman laser spectroscopy, X-ray powder diffraction, surface morphology, scanning electron microscopy (SEM). The free radical scavenging activity of the newly synthesized selenium (IV) complexes was determined at the concentration of 10, 20 and 30 ppm using stable DPPH free radicals. All complexes displayed a significant antioxidant activity.

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Conflict of Interests: The authors declare no conflict of interests.

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СИНТЕЗ, ОХАРАКТЕРИЗИРАНЕ И АНТИОКСИДАНТНА АКТИВНОСТ НА КОМПЛЕКСИ НА СЕЛЕН (IV) С НЯКОИ АМИНОКИСЕЛИНИ – БИНУКЛЕАРНИ КОМПЛЕКСИ

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(Резюме)

Получени са комплексите на селен (IV) с аминокиселините аспарагин (Asn), пролин (Pro), глутамин (Gln), метионин (Met) и цистеин (Cys) и са охарактеризирани чрез елементен анализ, измерване на молната проводимост, спектрални изследвания (IR, Раман, UV-Vis, 1H-NMR и мас-) и термогравиметричен анализ (TG/DTG). Изследванията на рентгеновата дифракция са проведени на дифрактометър PANalytical, повърхностната хомогенност на пробите е изследвана със сканиращ електронен микроскоп Quanta FEG 250 (SEM), а химичният състав на пробите е определен чрез енергийно-дисперсивен рентгенов анализ. Всички комплекси на селен (IV) (I-V) са от вида [Se(Asn)2Cl2], където AA = (Asn, Pro, Gln, Met и Cys) се отнасят като монобазични лиганди. Масовите фрагменти на комплекса [Se (Cys)2(Cl)2] (V) подкрепят твърдението за монобазичност. Предполагаемата геометрия на 1:2 комплексите е октаедрична конфигурация с два хлорни атома и два бидентатни лиганди, заемащи ъгловите места в октаедричните комплекси. В комплексите с аминокиселините комплекси на селен (IV) (I-V) амино и карбоксилните групи участват в координационен център с метал, докато Cys се координира посредством сулфидрилната и карбоксилната група. Активността на новосинтезираните комплекси на селен (IV) за отстраняване на свободни радикали е определена при концентрации от 10, 20 и 30 ppm въз основа на взаимодействието със стабилен свободен радикал 1,1-дифенил-2-пикрилхидразил (DPPH). Всички комплекси проявяват добра антиоксидантна активност.