

Synthesis, Crystal Structure, and Biological Properties of the Complex $[\text{Co}(\text{DmgH})_2(\text{Seu})_{1.4}(\text{Se-Seu})_{0.5}(\text{Se}_2)_{0.1}][\text{BF}_4]$

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Received June 21, 2016

Abstract—A new Co(III) dioxime complex with selenocarbamide was obtained by the reaction of $\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$, DmgH_2 , and Seu (DmgH_2 = dimethylglyoxime, Seu = selenocarbamide). According to X-ray diffraction (CIF file CCDC no. 1485732), the product was an ionic coordination compound with unusual composition, $[\text{Co}(\text{DmgH})_2(\text{Seu})_{1.4}(\text{Se-Seu})_{0.5}(\text{Se}_2)_{0.1}][\text{BF}_4]$ (I). Apart from two monodeprotonated DmgH^- molecules, the central atom coordinates neutral Seu , Se-Seu , and Se_2 molecules. Thus, the crystal contains the complex cations $[\text{Co}(\text{DmgH})_2(\text{Seu})_2]^+$, $[\text{Co}(\text{DmgH})_2(\text{Seu})(\text{Se-Seu})]^+$, and $[\text{Co}(\text{DmgH})_2(\text{Seu})(\text{Se}_2)]^+$. Each $[\text{BF}_4]^-$ anion is linked to the cations not only by electrostatic forces but also by intermolecular $\text{N}-\text{H}\cdots\text{F}$ hydrogen bonds (H-bonds). The complex cations are combined by intermolecular $\text{N}-\text{H}\cdots\text{O}$ H-bonds. The new coordination compound was found to possess biological activity. Treatment of the garlic (*Allium sativum* L.) foliage with an aqueous solution of I optimizes the content of selenium in the leaves and cloves and enhances the growth and plant productivity. The organs of treated plants are characterized by enhanced antioxidant protection owing to increasing activity of antioxidant enzymes and contents of proline and assimilation pigments, and decreasing lipid peroxidation.

Keywords: coordination compounds, cobalt dimethylglyoxime, selenocarbamide, X-ray diffraction, biological activity

DOI: 10.1134/S1070328417030046

INTRODUCTION

Cobalt(III) dioxime complexes are stable coordination compounds that can be used in biology and medicine [1, 2]. They also have useful properties in biological systems [3–5]. Previously, we prepared various Co(III) dioxime complexes with thiocarbamide [5–10] and made attempts to prepare such complexes with selenocarbamide. The composition of two of these compounds was determined: $[\text{Co}(\text{DmgH})_2(\text{Seu})_{1.75}(\text{Se-Seu})_{0.25}]_2[\text{TiF}_6] \cdot \text{H}_2\text{O}$ and $[\text{Co}(\text{DmgH})_2(\text{Seu})(\text{Se-Seu})]_2[\text{ZrF}_6] \cdot 3\text{H}_2\text{O}$ [11]. Along with selenocarbamide (Seu), these compounds contain a new ligand, Se-selenocarbamide (Se-Seu) (DmgH is monodeprotonated dimethylglyoxime). Subsequently we attempted the preparation of Co(III) dioxime complexes with selenocarbamide by the reaction of $\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$, DmgH_2 , and Seu . It was shown by X-ray diffraction that the reaction had given a new coordination compound with unusual composition, $[\text{Co}(\text{DmgH})_2(\text{Seu})_{1.4}(\text{Se-Seu})_{0.5}(\text{Se}_2)_{0.1}][\text{BF}_4]$ (I), in which the central atom coordinated neutral Seu , Se-Seu , and Se_2 (Se_2) molecules apart from

the two DmgH^- monoanions. According to published data [12], Seu was presumably converted in the reaction system to elemental selenium, which bound to both selenocarbamide to give Se-Seu and to itself to give Se_2 . A similar transformation was partially found earlier for Co(III) dimethylglyoximes containing $[\text{TiF}_6]^{2-}$ or $[\text{ZrF}_6]^{2-}$ anions [11]. Analysis of the Cambridge Crystallographic Data Centre [13] revealed one ruthenium compound with seleno-bis(1-methylimidazole-2-selenate), an organic ligand containing three Se atoms [14].

Since a primary goal of modern chemistry is development of more efficient technologies for various economy branches and selenium compounds are known to have a beneficial effect on garlic plants (*Allium sativum* L.) [15], one of the tasks is to prepare new coordination compounds for solving crop raising problems. Plant growth and productivity can be controlled by foliage spraying in the vegetation period; this is done by aqueous solutions of phytohormones, in particular, gibberellin [16]. Since foliage spraying with solutions of phytohormones is known to enhance

Table 1. Crystallographic data and X-ray experiment details for complex **I**

Parameter	Value
<i>M</i>	664.992
System	Triclinic
Space group	<i>P</i> 1
<i>a</i> , Å	7.9163(9)
<i>b</i> , Å	11.679(2)
<i>c</i> , Å	13.433(3)
α , deg	64.50(2)
β , deg	75.31(1)
γ , deg	82.05(1)
<i>V</i> , Å ³	1083.8(3)
<i>Z</i>	2
ρ (calcd.), g/cm ³	2.038
μ , mm ⁻¹	5.226
<i>F</i> (000)	648
Crystal size, mm	0.40 × 0.12 × 0.04
Range of θ , deg	3.07–25.05
Ranges of reflection indices	$-9 \leq h \leq 9$, $-9 \leq k \leq 13$, $-13 \leq l \leq 15$
Number of measured/unique reflections (<i>R</i> _{int})	5849/3803 (0.05320)
Filling, %	99.0
Number of reflections with <i>I</i> > 2 σ (<i>I</i>)	2454
Number of refined parameters	334
GOOF	1.005
<i>R</i> factor (<i>I</i> > 2 σ (<i>I</i>))	<i>R</i> ₁ = 0.0648, <i>wR</i> ₂ = 0.1591
<i>R</i> factor (whole set)	<i>R</i> ₁ = 0.0982, <i>wR</i> ₂ = 0.1935
$\Delta\rho_{\max}/\rho_{\min}$, e Å ⁻³	1.022/–0.686

plant growth owing to optimization of mineral nutrition and chlorophyll synthesis and increasing the antioxidant potential as a result of increasing selenium content, compound **I** was tested for biological activity.

EXPERIMENTAL

IR spectra were measured on a FT-IR Perkin-Elmer Spectrum 100 spectrometer in mineral oil in the 4000–400 cm⁻¹ range and ATR spectra were recorded in the 4000–650 cm⁻¹ range.

Synthesis of I. Dimethylglyoxime (0.23 g, 0.002 mol) in 40 mL of methanol and selenocarbamide (0.25 g, 0.002 mol) in 30 mL of methanol were added to $\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.34 g, 0.001 mol) in 30 mL of water. The resulting solution was heated for

10 min in a water bath in a graphite crucible at ~70°C. On slow evaporation, brown crystals precipitated from the dark brown solution (yield ~32%). The compound was soluble in alcohols and in water.

For $\text{C}_{9.9}\text{H}_{21.6}\text{BN}_{7.8}\text{O}_4\text{F}_4\text{Se}_{2.6}\text{Co}$

anal. calcd., %: C, 17.88; H, 3.27; N, 16.43.

Found, %: C, 17.56; H, 3.04; N, 16.19.

X-ray diffraction study of crystals **I** was carried out on a Xcalibur E diffractometer with a CCD array detector at room temperature (MoK_α radiation). The unit cell parameters refined for the whole set and the other experimental data were obtained using the Crys-Alis Oxford Diffraction program package [17]. The structure was solved by the direct method, the coordinates of non-hydrogen atoms were refined by the least-squares method in the anisotropic approximation (SHELX-97) [18]. The positions of hydrogen atoms attached to carbon or nitrogen were determined geometrically and refined isotropically in the rigid body model $B_H = 1.2U_X$ or $1.5U_X$ ($X = \text{C}, \text{N}$). The $[\text{BF}_4]^-$ anions are disordered and the coordinated Se-containing ligands partially occupy incomplete positiond (occupancy factors: one Seu molecule, 0.4; Se-Seu, 0.5; Se₂, 0.1). The key experimental and structure solution and refining details for **I** are summarized in Table 1, selected interatomic distances and bond angles are in Table 2, and the geometric parameters of H-bonds are in Table 3. The positions and thermal parameters for **I** are deposited with the Cambridge Crystallographic Data Centre (CCDC no. 1485732; www.ccdc.cam.ac.uk/conts/retrieving.html or deposit@ccdc.ca.ac.uk).

Biological studies. The selenium content in garlic plant leaves and bulbs were determined after annealing of freeze-dried samples in concentrated nitric acid and microwave extraction. Analysis was carried out on an AAnalyst 800 (Perkin Elmer) atomic absorption spectrometer with automatic sample injection (20 μL samples). Matrix modifier (5 μL) consisting of palladium ions was added into each sample by the autosampler [19]. Each sample was analyzed three times.

Garlic (*Allium sativum* L.) tends to accumulate trace mineral elements, including selenium; however, selenium content in the cloves depends on its content in soil and availability for plants. In this respect, the purpose of our experimental study was to identify the protective antioxidant potential of garlic plants treated with an aqueous solution of the new selenium-containing complex.

Garlic plants (*Allium sativum* L.) of the breed Izumrud cultured in the trial fields of the Institute of Genetics, Physiology, and Plant Protection, Academy of Sciences of Moldova, served as the investigation subjects. The field experiments were carried out in three blocks with randomized distribution.

Table 2. Interatomic distances and bond angles in the Co(III) coordination polyhedron of **I**

Bond	<i>d</i> , Å	Angle	ω , deg	Angle	ω , deg
Co(1)–N(1)	1.883(6)	N(1)Co(1)N(2)	80.9(3)	N(2)Co(1)Se(1)	93.8(1)
Co(1)–N(2)	1.896(6)	N(1)Co(1)N(3)	179.5(2)	N(2)Co(1)Se(2)	89.5(2)
Co(1)–N(3)	1.889(6)	N(1)Co(1)N(4)	98.7(3)	N(3)Co(1)N(4)	80.8(3)
Co(1)–N(4)	1.886(6)	N(1)Co(1)Se(1)	85.6(2)	N(3)Co(1)Se(1)	94.2(2)
Co(1)–Se(1)	2.429(1)	N(1)Co(1)Se(2)	94.6(2)	N(3)Co(1)Se(2)	85.6(2)
Co(1)–Se(2)	2.422(1)	N(2)Co(1)N(3)	99.6(3)	N(4)Co(1)Se(1)	88.4(2)
		N(2)Co(1)N(4)	177.8(2)	N(4)Co(1)Se(2)	88.3(2)
				Se(1)Co(1)Se(2)	176.67(5)

Table 3. Geometric parameters of intramolecular hydrogen bonds in structure **I**

D–H···A	Distance, Å	DHA angle, deg			Coordinates of A atoms
		D–H	H···A	D···A	
O(2)–H···O(3)	0.82	1.72	2.513(8)	161	<i>x, y, z</i>
O(4)–H···O(1)	0.82	1.75	2.524(8)	158	<i>x, y, z</i>
N(5)–H(1)···F(1)	0.86	2.24	2.98(1)	144	<i>x, y, z – 1</i>
N(5)–H(1)···F(7)	0.86	2.27	3.13(4)	176	<i>x, y, z – 1</i>
N(5)–H(2)···O(3)	0.86	2.03	2.892(9)	178	<i>x, y, z</i>
N(6)–H(1)···F(1)	0.86	2.18	2.94(1)	147	<i>x, y, z – 1</i>
N(6)–H(1)···F(8)	0.86	2.34	3.15(3)	156	<i>x, y, z – 1</i>
N(6)–H(2)···O(1)	0.86	2.09	2.920(9)	164	$-x, -y + 2, -z$
N(7)–H(1)···F(5)	0.86	2.13	2.92(4)	154	$x - 1, y, z$
N(7)–H(1)···F(6)	0.86	2.44	3.14(5)	138	$x - 1, y, z$
N(8)–H(1)···F(2)	0.86	2.06	2.86(3)	154	<i>x, y, z</i>
N(9)–H(1)···F(2)	0.86	2.03	2.71(3)	136	<i>x, y, z</i>
N(9)–H(2)···O(4)	0.86	2.24	3.07(2)	163	$x + 1, y, z$
N(10)–H(1)···F(3)	0.86	2.33	2.91(3)	125	$x - 1, y, z$

The experimental design implied monitoring of three blocks of plants: water-treated plants; plants treated with a gibberellin solution (125 mg/L); and plants treated with a solution of the new complex (40 µg Se/L). The planting density was 28 plants per m² and the plot area for each replication was 3 m². During the vegetation period, the foliage was treated with the specified solutions three times at 2-week intervals. The physiological processes in the leaves were analyzed after each treatment and those in cloves were assessed after the second and third treatments.

The antioxidant status was evaluated considering the change in the malondialdehyde (MDA) content and the activities of superoxide dismutase (SOD), catalase (CAT), ascorbate peroxidase (AP), glutathione reductase (GR), and glutathione peroxidase (GP). The lipid peroxidation intensity was assessed from the content of the final reaction product, MDA [20]. The

SOD activity was determined from the suppression of the photoreduction of tetrazolium nitroblue [21]. The amount of SOD needed for 50% suppression of tetrazolium nitroblue photoreduction was taken as the unit activity of the enzyme. The CAT activity was assessed from the decrease in the absorbance at 240 nm (molar extinction coefficient (ϵ) of 39.8 mmol⁻¹ cm⁻¹) [22]. The AP amount needed to oxidize ascorbate with decreasing absorbance at 290 nm (ϵ 2.8 mmol⁻¹ cm⁻¹) was taken as the unit activity of the enzyme [23, 24]. The GR activity was determined from the oxidation of NADPH₂ (reduced nicotinamide adenine dinucleotide phosphate) by measuring the absorbance of the solution at 340 nm [24], and the activity of GP was found from the oxidation of reduced glutathione by measuring the absorbance at 260 nm [25].

The results were statistically treated using the Statistica 7—ANOVA software.

RESULTS AND DISCUSSION

The IR spectrum of **I** exhibits stretching and bending absorption bands corresponding to the planar $\text{Co}(\text{DmgH})_2$ group (cm^{-1}): 2928 $\nu_{as}(\text{CH}_3)$, 2871 $\nu_s(\text{CH}_3)$, 1546 $\nu_{as}(\text{C}=\text{N})$, 1461 $\delta_{as}(\text{CH}_3)$, 1376 $\delta_s(\text{CH}_3)$, 1237 $\nu_{as}(\text{N}=\text{O})$, 1285 $\nu_s(\text{C}=\text{N})$, 1083 $\nu_s(\text{N}=\text{O})$, 972 $\gamma(\text{OH})$, 730 $\delta(\text{CNO})$, 507 $\nu_{as}(\text{Co}-\text{N})$, 428 $\nu_s(\text{Co}-\text{N})$. Complex **I** is a cobalt(III) *trans*-dioxime complex. The band corresponding to the $\delta(\text{NH}_2)$ mode is shifted to higher frequency (1631 cm^{-1}) with respect to that for free selenocarbamide, which is indicative of linking of Seu via NH_2 groups [26]. The $[\text{BF}_4]^-$ ions are located in the outer sphere of the complexes, as the bands at 1084 $\nu_{as}(\text{BF}_4)$, 761 $\nu_s(\text{BF}_4)$, and 524 cm^{-1} $\delta(\text{F}-\text{B}-\text{F})$ are present [27].

According to X-ray diffraction data, compound **I** is ionic and is formed by the $[\text{Co}(\text{DmgH})_2(\text{Seu})_{1.4}(\text{Se}-\text{Seu})_{0.5}(\text{Se}_2)_{0.1}]^+$ complex cation and the $[\text{BF}_4]^-$ anion. It was also ascertained that crystal **I** contains the $[\text{Co}(\text{DmgH})_2(\text{Seu})_2]^+$, $[\text{Co}(\text{DmgH})_2(\text{Seu})(\text{Se}-\text{Seu})]^+$, and $[\text{Co}(\text{DmgH})_2(\text{Seu})(\text{Se}_2)]^+$ cations (Fig. 1) with different occupancy factors. The Co(III) coordination octahedron is formed by four nitrogen atoms of two monodeprotonated DmgH^- ligands coordinated in the bidentate chelating fashion to give two metallacycles located in the equatorial plane of the octahedron. The axial sites of the octahedron are occupied by two Se atoms of different Se-containing ligands (Seu, Se-Seu, or Se-Se). Figure 1 shows the structure of the complex cations of **I**. The interatomic distances are the following: Co–N, 1.883(6)–1.896(6) Å; Co–Se, 2.429(1) and 2.422(1) Å (Table 2). The dihedral angle between the planes through the atoms of five-membered metallacycles is 2.4° , i.e., the equatorial moiety of the complex cation of **I** is nearly planar. The two DmgH^- ligands of the equatorial moiety are connected by intramolecular O–H···O H-bonds (O···O 2.513(8) and 2.524(8) Å) (Fig. 1, Table 3). This gives a 14-membered pseudomacrocyclic, which is typical of Co(III) complexes with dioximes [4–10, 28–31]. Interactions similar to those found in Co(III) dioximes with Thio or Seu occur between the metallacycles and the axial ligands in **I** [5–10]. The Seu ligand, which occurs in one fully occupied site, is linked to the equatorial DmgH^- ligand by an intramolecular N(5)–H···O(3) H-bond (N···O 2.892(9) Å) (Fig. 1, Table 3), while the Seu and Se-Seu ligands with site occupancy factors of 0.4 and 0.5, respectively, are connected to DmgH^- by $\pi\cdots\pi$ interactions.

In the crystal, a complex system of H-bonds is formed as a result of the presence of proton-donor amine groups in the complex cation and fluorine atoms of the $[\text{BF}_4]^-$ anions as the acceptors. Each $[\text{BF}_4]^-$ anion is connected to the complex cations, apart from electrostatic interactions, by intermolecular N–H···F H-bonds, while the cations are connected by intermolecular N–H···O H-

bonds (Fig. 2, Table 3). The $[\text{Co}(\text{DmgH})_2(\text{Seu})_2]^+$ complex cations are linked to form chains by two intermolecular H-bonds, N(6)–H···O(1) ($-x, -y + 2, -z$) and N(9)–H···O(4) ($x + 1, y, z$), while $[\text{Co}(\text{DmgH})_2(\text{Seu})_2]^+$, $[\text{Co}(\text{DmgH})_2(\text{Seu})(\text{Se}-\text{Seu})]^+$, and $[\text{Co}(\text{DmgH})_2(\text{Seu})(\text{Se}_2)]^+$ are combined only through the N(6)–H···O(1) ($-x, -y + 2, -z$) H-bonds.

It is known that under unfavorable environmental conditions, plants generate excess amounts of reactive oxygen species (ROS) and cells pass to the oxidative stress state, which disrupts the normal body homeostasis. The excess formation of ROS promotes lipid peroxidation, protein oxidation, destruction of nucleic acids, enzyme inhibition, and activation of programmed cell death [32]. It was demonstrated in many studies that selenium activates the protective antioxidant mechanisms and reduces the oxidative stress [33]. It is believed that the protective action of selenium in the oxidative stress is expressed as decreasing content of MDA, increasing free proline level and chlorophyll stability, and biomass accumulation. The selenium action in plants is related to the formation of the active sites of antioxidant system enzymes (superoxide dismutase, glutathione reductase, glutathione peroxidase, catalase, ascorbate peroxidase, and dehydroascorbate reductase) and to increase in the content of some small-molecule antioxidants: carotenoids, ascorbic acid, glutathione.

Our results confirm the data that selenium increases the antioxidant activities of plants. Treatment of the garlic plant foliage (*Allium sativum* L.) with an aqueous solution of the complex $[\text{Co}(\text{DmgH})_2(\text{Seu})_{1.4}(\text{Se}-\text{Seu})_{0.5}(\text{Se}_2)_{0.1}]^+[\text{BF}_4]$, conventionally called Fludisec, was found to enhance the antioxidant protection of cells by increasing the activity of antioxidant enzymes (Table 4).

Higher contents of MDA were found in the leaves and cloves of control plants: 32.35 ± 0.38 and 16.18 ± 0.20 mmol per gram of dry sample, whereas in the gibberellins-treated plants, the MDA content decreased by 13.08 and 7.18% in the leaves and cloves, respectively. On treatment with Fludisec, the content of MDA decreased by 21.11 in the cloves and by 25.15% in the leaves with respect to the control plants (Table 4).

The treatment of plants with either gibberellin or biologically active complex **I** led to substantial increase in the activity of antioxidant protection enzymes (Table 4). In these plants, ascending trends were observed for SOD, CAT, AP, GP, and GR activities in both leaves and cloves. The antioxidant effect of Fludisec is manifested as a decrease in the MDA content and enhancement of the antioxidant protection enzyme activity in comparison with not only control plants but also the plants treated with gibberellin. The treatment of plants with an aqueous solution of the new selenium-containing complex resulted in

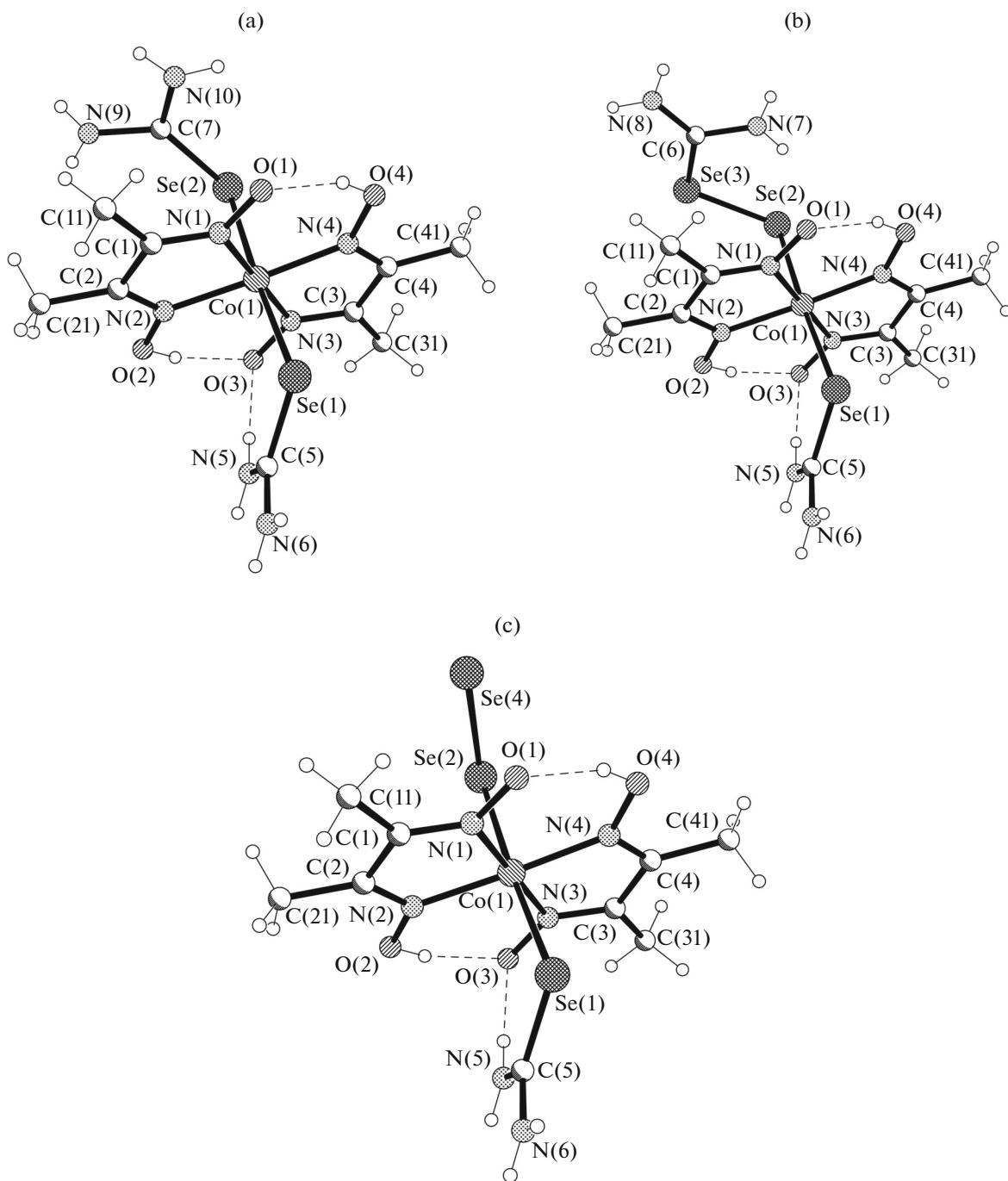


Fig. 1. Structure of the complex cations in I: (a) $[\text{Co}(\text{DmgH})_2(\text{Seu})_2]^+$, (b) $[\text{Co}(\text{DmgH})_2(\text{Seu})(\text{Se-Seu})]^+$, and (c) $[\text{Co}(\text{DmgH})_2(\text{Seu})(\text{Se}_2)]^+$.

increased content of assimilation pigments in the leaves (Table 5).

The gibberellin-treated plants had higher (by 17.61%) content of green pigment compared with the control. The plants treated with Fludisec had a 24.81% higher content of chlorophylls. The content of carotenoids, which also perform antioxidant protection of

chloroplasts from the oxidative destruction, also markedly increased.

The protective action of the new cobalt complex is also manifested in the increased content of proline (Table 6), a compound with numerous protective functions for plants affected by adverse factors, in particular, it performs osmoregulation, stabilizes cell and membrane structures, and neutralizes free radicals.

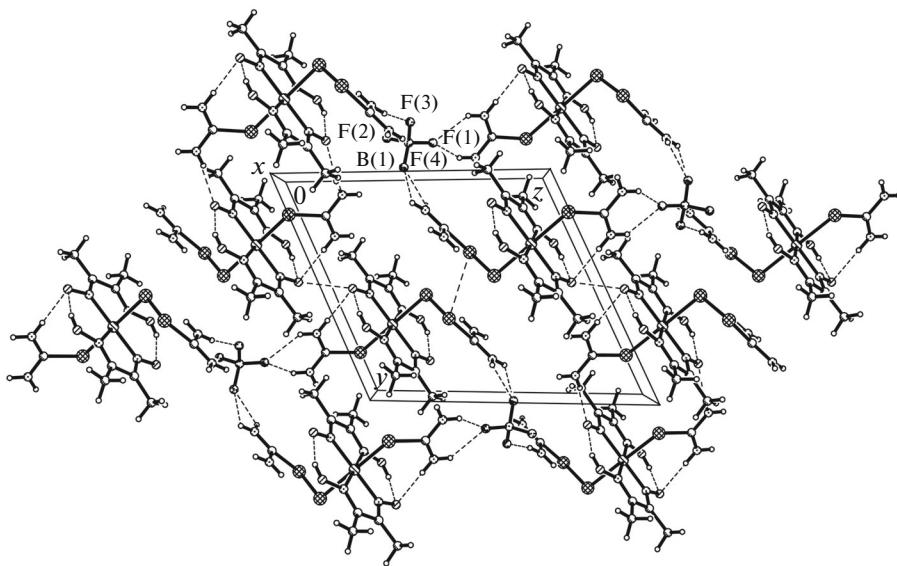


Fig. 2. Fragment of the crystal structure of I.

The increase in the activity of antioxidant protection systems in garlic plant leaves and cloves is a consequence of increasing selenium content in the cells (Table 7).

The most pronounced increase in the selenium content was detected in the organs of Fludisec-treated

plants. Optimization of the functional state of plants treated with gibberellin and, especially, Fludisec stimulated the growth and productivity (Table 8). The accumulation of biomass by the plants treated with gibberellin and, especially, Fludisec is much higher than that for control plants. The plant weight gain was

Table 4. Malondialdehyde content and activity of antioxidant protection enzymes in the leaves of cloves of garlic plants (*Allium sativum* L.)

Parameters	Control	Gibberellin, 125 mg L ⁻¹		Fludisec, 0.00001%	
	<i>M</i> ± <i>m</i> *	<i>M</i> ± <i>m</i>	Δ, % to the control	<i>M</i> ± <i>m</i>	Δ, % to the control
Leaves (after the 3rd treatment)					
MDA, μM g ⁻¹ w.s.**	32.35 ± 0.38	28.12 ± 0.29	-13.08	25.52 ± 0.36	-21.11
SOD, arb.u. g ⁻¹ w.s.	62.81 ± 0.73	66.86 ± 0.92	6.45	78.39 ± 0.47	24.80
CAT, mM g ⁻¹ w.s.	1.30 ± 0.015	1.78 ± 0.009	36.92	1.94 ± 0.04	49.23
AP, mM g ⁻¹ w.s.	8.43 ± 0.13	9.62 ± 0.17	14.12	12.44 ± 0.35	47.57
GR, mM g ⁻¹ w.s.	172.8 ± 2.08	195.31 ± 4.27	13.00	118.30 ± 2.12	38.46
GP, mM g ⁻¹ w.s.	85.44 ± 1.94	106.58 ± 2.15	24.74	217.01 ± 3.64	25.56
Cloves (after the 3rd treatment)					
MDA, μM g ⁻¹ w.s.	16.18 ± 0.20	15.18 ± 0.34	-7.18	12.1 ± 0.19	-25.15
SOD, arb.u. g ⁻¹ w.s.	52.81 ± 0.77	57.86 ± 0.61	9.56	70.14 ± 0.52	32.82
CAT, mM g ⁻¹ w.s.	2.14 ± 0.012	2.32 ± 0.07	8.41	2.98 ± 0.05	39.25
AP, mM g ⁻¹ w.s.	7.16 ± 0.10	8.57 ± 0.14	19.69	11.31 ± 0.02	57.96
GR, mM g ⁻¹ w.s.	182.84 ± 2.95	205.31 ± 5.62	12.29	227.01 ± 3.89	24.16
GP, mM g ⁻¹ w.s.	95.15 ± 2.31	101.34 ± 1.86	6.51	120.21 ± 2.05	26.34

* *M* is the arithmetic mean; *m* is the error of mean.

** w.s. is wet sample.

Table 5. Effects of gibberellin and Fludisec on the pigment content in garlic leaves

Versions	Chlorophyll <i>a</i> , mg/100 g w.s.		Chlorophyll <i>b</i> , mg/100 g w.s.		Chlorophyll <i>a + b</i> , mg/100 g w.s.		Carotenoids, mg/100 g w.s.	
	<i>M</i> ± <i>m</i>	Δ, % to the control	<i>M</i> ± <i>m</i>	Δ, % to the control	<i>M</i> ± <i>m</i>	Δ, % to the control	<i>M</i> ± <i>m</i>	Δ, % to the control
Control	20.21 ± 0.51		9.49 ± 0.16		29.70 ± 0.66		8.76 ± 0.20	
Gibberellin, 125 mg L ⁻¹	23.81 ± 0.62	17.81	11.11 ± 0.28	17.07	34.93 ± 0.81	17.61	10.13 ± 0.22	15.64
Fludisec 0.00001%	25.17 ± 0.54	24.54	11.78 ± 0.29	24.13	37.07 ± 0.66	24.81	10.30 ± 0.17	17.58

Table 6. Proline content (μg/g w.s.) in the garlic plant leaves and cloves (*Allium sativum* L.), treated with gibberellin and Fludisec

Organ	Control	Gibberellin, 125 mg/L		Fludisec 0.00001%	
	<i>M</i> ± <i>m</i>	<i>M</i> ± <i>m</i>	Δ, % control	<i>M</i> ± <i>m</i>	Δ, % control
Leaves	0.240 ± 0.006	0.293 ± 0.008	22.08	0.410 ± 0.013	70.83
Cloves	1.735 ± 0.047	1.850 ± 0.038	6.63	2.247 ± 0.052	29.51

Table 7. Effect of garlic plant (*Allium sativum* L.) treatment on the selenium content in the leaves and cloves (μg/kg w.s.)

Organ	Control	Gibberellin, 125 mg/L		Fludisec 0.00001%	
	<i>M</i> ± <i>m</i>	<i>M</i> ± <i>m</i>	Δ, % control	<i>M</i> ± <i>m</i>	Δ, % control
Leaves	74.0 ± 1.8	84.0 ± 2.1	13.51	88.0 ± 1.9	18.92
Cloves	47.0 ± 0.7	59.0 ± 1.2	25.53	70.0 ± 1.1	48.94

Table 8. Effects of gibberellin and Fludisec on the productivity of garlic plants (*Allium sativum* L.)

Versions	Plant weight, g		Productivity, g/p.*		Crop, kg/m ²	
	<i>M</i> ± <i>m</i>	Δ, %	<i>M</i> ± <i>m</i>	Δ, %	<i>M</i> ± <i>m</i>	Δ, %
Control	64.44 ± 0.82		36.289 ± 0.73		1.016 ± 0.09	
Gibberellin, 125 mg L ⁻¹	68.87 ± 1.08	6.87	39.000 ± 0.58	7.47	1.092 ± 0.13	7.48
Fludisec 0.00001%	78.10 ± 0.74	21.20	44.34 ± 0.64	22.20	1.241 ± 0.08	22.18

* g/p. is g/plant.

6.87 and 21.20%, respectively. The average weight of cloves is 7.47 and 22.20% greater upon gibberellin and Fludisec treatment, respectively. Treatment of the plants with the new complex provided a crop gain of 22.18% relative to the control and 13.70% relative to the gibberellin-treated plants.

Thus, compound **I** is biologically active. Treatment of the garlic plant (*Allium sativum* L.) foliage with an aqueous solution of **I** optimizes the selenium content in the leaves and cloves and enhances the plant growth and productivity. The organs of treated plants have enhanced antioxidant protection as a result of increas-

ing activity of antioxidant enzymes, increasing proline and assimilation pigment contents, and suppression of lipid peroxidation.

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Translated by Z. Svitanko