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Cobalt(III) Dimethylglyoximates Containing Selenourea and an Unusual Diselenourea Ligand: Synthesis and Structures

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Abstract—The complexes $[Co(DH)_2(Seu)_y(Se-Seu)_z]_2X \cdot mSolv$ (DH is the dimethylglyoxime monoanion, Seu is selenourea, and X is $[TiF_6]^{2-}$, $[ZrF_6]^{2-}$) were obtained from the system $CoX \cdot 6H_2O-DH_2$ –Seu in DMF–MeOH or MeOH–H₂O and examined by UV, IR, and NMR spectroscopy and X-ray diffraction. Unexpectedly, the ligand Se-Seu (the oxidized form of selenourea) was detected on the axial coordinate, partially replacing selenourea. The complexes were formulated as $[Co(DH)_2(Seu)_{1.75}(Se-Seu)_{0.25}]_2[TiF_6] \cdot H_2O$ (I) and $[Co(DH)_2(Seu)(Se-Seu)]_2[ZrF_6] \cdot 3H_2O$ (II). The complex cations in I and II have *trans*-octahedral

structures. Their crystal structures are made up of the complex Co^{3+} cations and the outer-sphere MF_6^{2-} anions (M = Ti(IV) (I) and Zr(IV) (II)) held together by electrostatic interactions and hydrogen bonds; water of crystallization is also involved in hydrogen bonding.

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The formation of stable chelate complexes is a crucial factor for use of α -dioximes in the synthesis of transition metal complexes [1, 2]. The presence of various axial ligands in octahedral α -dioximates creates prerequisites for variation of the composition and revealing of the structural features and novel properties of the resulting complexes [2-5]. In the last few years, interest in finding correlations between the composition, structure, and biological properties of compounds has been increased. Much importance is attached to the stability of complexes, which depends on the electron-donating atom of the ligand coordinating the complexing metal in axial positions. In the study of the thermal stability and decomposition of Co(III) dioximates containing both thiourea (Thio) and selenourea (Seu) [6], it has been found that the decomposition of these complexes involves a number of exothermic processes and that the Thio-containing dioximates are more stable than their Seu-containing analogs (e.g., T_{decomp} of $[\text{Co}(\text{DH})_2(\text{Thio})_2]\text{NO}_3$ is higher by ~50°C than T_{decomp} of $[\text{Co}(\text{DH})_2(\text{Seu})_2]\text{NO}_3$.

Recent studies [7, 8] have revealed that Co(III) dioximates can act as stimulators of the biosynthesis of enzymes by some microfungi strains. Addition of such complexes in certain amounts to nutrient media of these microorganisms increases the productivity and, in some cases, reduces the cultivation cycle of the producer [10]. According to experimental data [11, 12],

Thio-containing cobalt dioximates exhibit biological activity; apparently, their Seu analogs can also be biologically active. Selenourea has been tested with *Escherichia Coli* and found to be nontoxic in a concentration below 0.1 mol/l [13]. In addition, reactions of Se-containing molecules with some oxidants can give nanoselenium particles with enhanced biochemical activity [14–17].

Literature data on Seu-containing cobalt(III) dioximates are scarce. Apparently, their configurations are believed to be similar to Thio-containing analogs. In the Cambridge Crystallographic Data Collection [18], we managed to retrieve only one structure of this type: $NH_4[Co(DH)_2(SeCN)_2]$ [19].

In the targeted synthesis from the system CoX \cdot 6H₂O–DH₂–Seu in DMF–MeOH or MeOH–H₂O, we obtained complexes of the general formula [Co(DH)₂(Seu)_y(Se-Seu)_z]₂X · mSolv, where DH is the dimethylglyoxime monoanion and X is [TiF₆]^{2–}, [ZrF₆]^{2–}. The compositions and structures of these complexes were examined using modern physical techniques. A single-crystal X-ray diffraction study revealed that Seu molecules on one axial coordinate of the complex cations are replaced partially or fully by the ligand Se-Seu, which is an oxidation product from selenourea. The complexes obtained can be formulated as [Co(DH)₂(Seu)_{1.75}(Se-Seu)_{0.25}]₂[TiF₆] · H₂O (I) and [Co(DH)₂(Seu)(Se-Seu)]₂[ZrF₆] · 3H₂O (II). The

coordination of Se-Seu in dioximates was detected for the first time. Although the oxidation of Seu and Thio is known to produce dications or elemental selenium or sulfur, this effect has not been discovered in similar Thio-containing complexes [20-22]. Apparently, this is because Seu oxidizes more easily than Thio [23].

EXPERIMENTAL

Synthesis of complex I. A cobalt(III) compound was prepared by oxidation of cobalt(II) with atmospheric oxygen. A solution of CoTiF₆ · $6H_2O$ (0.33 g, 1 mmol) in water (30 ml) was added dropwise to a warm (~60°C) solution of dimethylglyoxime (0.23 g, 2 mmol) and selenourea (0.25 g, 2 mmol) in methanol (40 ml). Dropwise addition was required to prevent abrupt cooling of the solution. Then the solution was heated on for 10–15 min, filtered, and left for slow evaporation at room temperature. The resulting dark brown prismatic crystals were isolated. The yield of complex I was ~25%. Complex I is soluble in DMF, DMSO, and alcohols but is less soluble in water.

For $C_{20}H_{46}Co_2F_6N_{16}O_9Se_{4.5}Ti$					
anal. calcd., %:	C 18.63;	Н 3.59;	N 17.38.		
Found, %:	C 18.29;	H 3.51;	N 17.04.		

Complex II was obtained as described for complex I. Cherry-colored crystals as needle-like rectangles were isolated from the resulting dark brown solution. The yield of complex **II** was ~30%. Complex **II** is soluble in DMF, DMSO, and alcohols but is less soluble in water.

For $C_{20}H_{50}Co_2F_6N_{16}O_{11}Se_6Zr$					
anal. calcd., %:	C 16.15;	H 3.39;	N 15.07.		
Found, %:	C 15.89;	Н 3.24;	N 14.83.		

IR spectra were recorded on FT-IR 100 (4000–400 cm⁻¹), ATP (4000–650 cm⁻¹), and SPECORD M80 spectrometers (400–250 cm⁻¹) in Nujol. UV spectra were recorded on a Perkin Elmer Lambda 25 spectrophotometer in aqueous solutions ($0.5 \times 10^{-4} \text{ mol/l}$). ¹H and ¹³C NMR spectra were recorded on a Bruker Avance DRX 400 spectrometer (400.13 (¹H) and 100.61 MHz (¹³C)) in DMSO-d₆ with TMS as the internal standard. ¹⁹F NMR spectra were recorded on a Bruker AC-200 spectrometer in D₂O.

An X-ray diffraction study was performed at room temperature on Bruker SMART APEX (for I) and Xcalibur, Eos Oxford Diffraction diffractometers (for II) fitted with CCD detectors (graphite monochromator, Mo K_{α} radiation, $\lambda = 0.71073$ Å, ω scan mode). The structures were solved by direct methods and refined by the least-squares method in the anisotropic full-matrix approximation (on F^2) for non-hydrogen atoms (SHELX-97) [24]. The positions of the oxime H atoms were partially determined from difference electron-density maps; the others were located geometrically and refined isotropically using a rigid-body model. The H atoms of water molecules were not located because they are disordered over several positions. In complex I, one Seu molecule and one Se-Seu molecule are disordered in two positions (0.75/0.25). In both structures, the anions are disordered over several positions ($[TiF_6]^{2-}$ in I and $[ZrF_6]^{2-}$ in II).

The crystallographic parameters and the data collection and refinement statistics for structures I and II are summarized in Table 1. Bond lengths and bond angles are listed in Table 2. The geometrical parameters of the hydrogen bonds are given in Table 3. Atomic coordinates and thermal parameters for structures I and II have been deposited with the Cambridge Crystallographic Data Collection (nos. 789 756 (I) and 789757 (II); deposit@ccdc.cam.ac.uk or http://www. ccdc.cam.ac.uk/data_request/cif).

RESULTS AND DISCUSSION

According to elemental analysis data, the reactions of DH₂ and Seu cobalt salt with $[TiF_6]^{2-}$ and $[ZrF_6]^{2-}$ could be assumed to give ionic compounds made up of the complex Co³⁺ cation containing two DH⁻ residues and two Seu molecules and the corresponding anions. The crystals of complexes I and II contain water of crystallization. This type of complexes is characterized by the presence of solvent (normally, water) molecules in the crystal structure, which form a complicated system of hydrogen bonds sometimes giving rise to supramolecular frameworks [25].

The UV spectra of complexes I and II show two absorption bands at 200–400 nm. The first band provides evidence for the presence of dioxime in the equatorial plane and is due to the π – π *-transition in the fragment Co(DH)₂; the second band confirms the presence of the coordinated selenourea. As with Thiocontaining dioximates, the absorption band corresponding to the coordinated Seu molecule becomes less intense with time in solutions of complexes I and II, which suggests replacement of the apical ligand by a solvent molecule.

The IR spectra of complexes I and II contain absorption bands at 1570–1580 (v(CN)), 1230–1240 and 1080–1095 (v(NO)), and 505–525 and 425–440 cm⁻¹ (v(Co–N)); this proves the coordination of the dimethylglyoxime monoanion to the complexing metal [26].

The IR spectra of complexes I and II show absorption bands characteristic of selenourea; most of them are combinations of several vibrations: 3400-3200, 1640-1600, 1400-1370, 1100-1070, 630-610, and 400-380 cm⁻¹. An analysis of the vibrations of Seu molecules and complexes of some metals with Seu [27, 28] allows these bands to be assigned as follows: $v_{as,s}$ (NH), δ (NH₂), <u>HNC</u> + CSe + CN + NCN + NCSe, <u>HNC</u> + CN + CSe, δ <u>NCN</u> + CSe + NCSe, and <u>CSe</u> + NCN (the types of vibrations with dominant contributions are underlined). The last band at

Parameter	Value			
T atameter	Ι	II		
М	1289.81	1487.60		
Т, К	297(2)	293(2)		
Crystal system	Triclinic	Triclinic		
Space group	$P\overline{1}$	$P\overline{1}$		
Unit cell parameters				
<i>a</i> , Å	8.082(1)	7.9721(6)		
<i>b,</i> Å	11.580(2)	11.521(1)		
<i>c,</i> Å	13.318(2)	14.190(1)		
α, deg	66.389(3)	69.472(8)		
β, deg	79.236(3)	86.001(7)		
γ, deg	81.231(3)	82.188(7)		
<i>V</i> , Å ³	1117.8(3)	1208.9(2)		
Ζ	1	1		
ρ_{calcd} , g/cm ³	1.916	2.043		
μ , mm ⁻¹	4.656	5.492		
<i>F</i> (000)	633	722		
Crystal dimensions, mm	0.2 imes 0.2 imes 0.15	0.2 imes 0.15 imes 0.1		
θ scan range, deg	2.02-25.50	2.97-25.50		
Ranges of h , k , and l indices	$-9 \le h \le 9$	$-9 \le h \le 9$		
	$-14 \le k \le 14$	$-11 \le k \le 13$		
	$-16 \le l \le 16$	$-16 \le l \le 17$		
Number of measured/independent reflections	$11225/4136 \ (R_{\rm int} = 0.0420)$	$7821/4481 \ (R_{\rm int} = 0.0391)$		
Filling for $\theta = 25.50, \%$	99.3	99.7		
Number of reflections with $I > 2\sigma(I)$	3236	2695		
Number of parameters refined	292	302		
GOOF	0.977	1.020		
<i>R</i> factor $(I > 2\sigma(I))$	$R_1 = 0.0656, wR_2 = 0.1773$	$R_1 = 0.0699, wR_2 = 0.2064$		
<i>R</i> factor (for all reflections)	$R_1 = 0.0861, wR_2 = 0.1905$	$R_1 = 0.1082, wR_2 = 0.2167$		
$\Delta \rho_{\rm max}, \Delta \rho_{\rm min}, e {\rm \AA}^{-3}$	0.839, -0.786	1.086, -1.722		

Table 1. Crystallographic parameters and the data collection and refinement statistics for structures I and II

400-380 cm⁻¹ is mainly contributed by the CSe vibrations [28]; its position is constant in the spectra of all the complexes studied.

The band $\delta(NH_2)$ in the spectra of complexes I and II is shifted to the higher frequencies (1640–1600 cm⁻¹) compared to the corresponding band of free selenourea. Therefore, Seu is involved in hydrogen bonding through the NH₂ groups [26]. The constant position of the band at 400–380 cm⁻¹ and the absorption bands due to the M–Se vibrations below 200 cm⁻¹ [28] precluded recording and identification of the bands corresponding to the Se–Se, M–Se, and M–Se–C vibrations.

In the ¹H NMR spectra of complexes I and II, the signals $\delta(CH_3)$ are shifted downfield from 1.96 to 2.2–2.4 ppm because of the electron density transfer from

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the dimethylglyoxime ligand to the complexing metal [29]. The methyl groups in complexes I and II are manifested as a singlet; hence, they are magnetically equivalent and both complexes have a *trans*-configuration [30, 31]. A signal at δ 11.4 ppm for the OH group is shifted downfield (δ 17.72 ppm), thus confirming intramolecular hydrogen bonding. Signals at δ 8.10–8.45 ppm correspond to the amino groups of Seu. Although only one signal for the methyl groups of the fragment Co(DH)₂⁺ should be expected, the spectrum shows more signals (i.e., the solution contains several types of complexes).

It is known that the ¹³C NMR spectra exhibit two signals for DH₂ at δ 9.2 and 153.1 ppm corresponding to the C¹(C⁴) and C²(C³) atoms [32]. In the spectra of

2011

No. 10

Complex cations							
David	d, Å		Dand		d, Å		
Bond	Ι	II	Bond	Ι	II		
Co(1)–N(1)	1.885(6)	1.868(8)	C(1)–C(3)	1.46(1)	1.44(2)		
Co(1) - N(2)	1.889(5)	1.910(8)	C(3) - C(4)	1.49(1)	1.50(2)		
Co(1) - N(3)	1.890(6)	1.882(8)	C(5) - C(6)	1.52(1)	1.50(2)		
Co(1) - N(4)	1.887(6)	1.900(8)	C(5) - C(7)	1.44(1)	1.43(2)		
Co(1)-Se(1)	2.41(1)		C(7) - C(8)	1.50(1)	1.53(2)		
Co(1)-Se(1A)	2.49(3)	2.422(2)	Se(1)-C(9)	1.88(2)			
Co(1)-Se(2)	2.413(1)	2.428(2)	C(9) - N(5)	1.29(2)			
O(1) - N(1)	1.361(8)	1.408(9)	C(9) - N(6)	1.34(2)			
O(2) - N(2)	1.348(8)	1.300(10)	Se(1A)-Se(1B)	2.19(3)	2.282(2)		
O(3) - N(3)	1.335(8)	1.368(9)	Se(1B)-C(9A)	1.95(4)	1.87(2)		
O(4) - N(4)	1.343(8)	1.333(9)	C(9A) - N(5A)	1.32(5)	1.20(2)		
N(1) - C(1)	1.284(9)	1.28(1)	C(9A) - N(6A)	1.39(5)	1.33(3)		
N(2) - C(3)	1.29(1)	1.30(1)	Se(2)-C(10)	1.874(7)	1.866(9)		
N(3) - C(5)	1.30(1)	1.27(1)	C(10) - N(7)	1.294(9)	1.37(1)		
N(4) - C(7)	1.305(9)	1.29(1)	C(10) - N(8)	1.325(9)	1.28(1)		
C(1)–C(2)	1.51(1)	1.48(1)		~ /			
Angle	ω,	ω, de		ω, deg			
Angle	Ι	II	Aligie	Ι	II		
N(1)Co(1)N(2)	81.0(3)	80.5(3)	C(7)N(4)O(4)	119.9(7)	121.5(8)		
N(1)Co(1)N(3)	99.0(3)	101.0(3)	C(7)N(4)Co(1)	116.4(5)	115.4(7)		
N(1)Co(1)N(4)	178.0(3)	176.6(3)	O(4)N(4)Co(1)	123.7(5)	123.1(6)		
N(2)Co(1)N(3)	179.6(3)	178.4(3)	N(1)C(1)C(2)	123.9(8)	123.1(9)		
N(2)Co(1)N(4)	98.6(3)	97.9(3)	N(1)C(1)C(3)	112.7(7)	111.9(9)		
N(3)Co(1)N(4)	81.4(3)	80.7(3)	C(2)C(1)C(3)	123.3(7)	124.9(10)		
N(1)Co(1)Se(1)	88.4(3)		N(2)C(3)C(1)	112.5(6)	113.7(10)		
N(2)Co(1)Se(1)	94.3(3)		N(2)C(3)C(4)	123.6(8)	120.2(11)		
N(3)Co(1)Se(1)	86.1(3)		C(1)C(3)C(4)	123.8(8)	126.1(10)		
N(4)Co(1)Se(1)	89.7(3)		N(3)C(5)C(6)	121.6(8)	121.3(10)		
N(1)Co(1)Se(1A)	94.3(7)	90.7(2)	N(3)C(5)C(7)	113.7(6)	113.2(10)		
N(2)Co(1)Se(1A)	92.7(8)	93.5(2)	C(6)C(5)C(7)	124.6(8)	125.3(10)		
N(3)Co(1)Se(1A)	87.7(8)	87.1(2)	N(4)C(7)C(5)	112.5(6)	113.7(9)		
N(4)Co(1)Se(1A)	83.7(7)	86.4(2)	N(4)C(7)C(8)	123.2(8)	121.9(10)		
N(1)Co(1)Se(2)	94.9(2)	95.0(2)	C(5)C(7)C(8)	124.3(8)	124.3(10)		
N(2)Co(1)Se(2)	85.7(2)	85.4(2)	C(9)Se(1)Co(1)	109(1)			
N(3)Co(1)Se(2)	94.0(2)	93.9(2)	N(5)C(9)N(6)	114(2)			
N(4)Co(1)Se(2)	87.1(2)	87.9(2)	N(5)C(9)Se(1)	127(2)			
Se(1)Co(1)Se(2)	176.7(2)	173.94(6)	N(6)C(9)Se(1)	117(1)			
Se(2)Co(1)Se(1A)	170.3(7)		C(9A)Se(1B)Se(1A)	91(2)	100.9(8)		
C(1)N(1)O(1)	118.8(6)	118.9(8)	Se(1B)Se(1A)Co(1)	104(1)	108.35(6)		
C(1)N(1)Co(1)	117.0(5)	118.7(6)	N(5A)C(9A)N(6A)	116(4)	119(2)		
O(1)N(1)Co(1)	124.1(5)	122.4(6)	N(5A)C(9A)Se(1B)	128(3)	122(2)		
C(3)N(2)O(2)	121.2(6)	122.0(9)	N(6A)C(9A)Se(1B)	115(3)	119(2)		
C(3)N(2)Co(1)	116.7(5)	115.2(7)	C(10)Se(2)Co(1)	112.2(2)	113.6(3)		
O(2)N(2)Co(1)	122.0(4)	122.8(6)	N(7)C(10)N(8)	119.4(7)	119.7(8)		
C(5)N(3)O(3)	122.0(6)	122.2(9)	N(7)C(10)Se(2)	125.8(5)	123.4(7)		
C(5)N(3)Co(1)	115.9(5)	117.0(7)	N(8)C(10)Se(2)	114.7(5)	116.9(7)		
O(3)N(3)Co(1)	122.1(4)	120.8(6)					

 Table 2. Selected bond lengths and bond angles in structures I and II

Table 2. (Contd.)

Complex anions						
Dand		d, Å				
Dolla	I (Ti(1))	I (Ti(2))	II (Zr(1))	II (Zr(1A))		
M(1)-F(1)	1.82(2)	1.82(2)	1.98(1)	1.98(2)		
M (1)-F(2)	1.97(3)	1.80(2)	2.03(2)	2.00(2)		
M(1)-F(3)	1.73(2)	1.82(2)	1.98(1)	1.97(2)		
M(1)-F(4)		1.82(2)	1.96(2)	1.99(2)		
M(1)-F(5)		1.81(2)	1.99(1)	1.98(2)		
M(1)-F(6)		1.81(2)	1.99(1)	1.99(2)		
Amala		ω,	deg			
Angle	I (Ti(1))	I (Ti(2))	II (Zr(1))	II (Zr(1 <i>A</i>))		
F(1)M(1)F(2)	92.7(10)	179.1(8)	87.6(6)	85(1)		
F(1)M(1)F(3)	86.4(9)	89.1(6)	90.6(6)	94(1)		
F(1)M(1)F(4)		90.4(6)	176.8(7)	173(2)		
F(1)M(1)F(5)		89.7(6)	91.8(6)	93(1)		
F(1)M(1)F(6)		89.3(6)	90.8(6)	90(1)		
F(2)M(1)F(3)	96(1)	91.2(6)	89.6(6)	91(1)		
F(2)M(1)F(4)		90.4(6)	89.3(6)	89(1)		
F(2)M(1)F(5)		90.0(6)	179.1(7)	177(2)		
F(2)M(1)F(6)		89.8(6)	88.7(6)	88(1)		
F(3)M(1)F(4)		89.1(8)	89.9(6)	90(1)		
F(3)M(1)F(5)		178.4(8)	91.0(6)	92(2)		
F(3)M(1)F(6)		90.3(7)	177.7(7)	177(2)		
F(4)M(1)F(5)		89.8(7)	91.4(6)	93(1)		
F(4)M(1)F(6)		179.4(9)	88.6(6)	86(1)		
F(5)M(1)F(6)		90.7(7)	90.8(6)	90(1)		

complexes I and II with DH⁻, the signal for the methyl C atom is shifted downfield (δ 11.19–11.37 ppm), while the signal for the quaternary C atoms is shifted upfield (δ 148.38–151.76 ppm). This is due to the electron density redistribution upon the coordination of dimethylglyoxime to the central atom. As with the ¹H NMR spectra, only one signal for the methyl groups of the fragment $Co(DH)_2^+$, should be expected to appear in the ¹³C NMR spectra; however, the presence of more signals confirms the formation of several types of complexes. For complexes I and II, it is assumed that one apical molecule slants toward the pseudoaromatic chelate ring in the equatorial plane since the quaternary C atoms are manifested by a pair of signals corresponding to some different "chemical types". Free selenourea is characterized by a signal at δ 178.91. The ¹³C NMR spectrum should contain only one higher-field signal ($\delta 166-172$) for the coordinated Seu molecule; in most cases, however, this spectral range exhibits several signals.

The ¹⁹F NMR spectra of complexes I and II show one signal for the outer-sphere anion: $\delta \sim 72$ ([TiF₆]^{2–}) and -13.7 ([ZrF₆]^{2–}). The presence of only one signal in the spectrum suggests that all F atoms are magnetically equivalent and that the complex anions are stable in solution.

Although the crystals of most of the novel selenourea-containing dioximates are unstable in air, we isolated crystals of two representatives of this series with DH⁻ (complexes I and II). Both complexes have an ionic character. According to X-ray diffraction data, structure I contains two types of the complex cations $[Co(DH)_2(Seu)_2]^+$ and $[Co(DH)_2(Seu)(Se Seu)]^+$ (Fig. 1a) in a ratio of 3 : 1, the $[TiF_6]^{2-}$ anions with the Ti atoms occupying two crystallographic positions (in the center of inversion and in a general position), and molecules of water of crystallization. In structure II, the complex cations $[Co(DH)_2(Seu)(Se Seu)]^+$, the $[ZrF_6]^-$ anions disordered in two positions, and water molecules are stabilized only (Fig. 1b). In the cation of the second type, the novel ligand Se-Seu

Contact D. HA	Distance, Å			Angle DUA deg	Coordinates of stoms A
Contact D=11 A	D-H	H A	D A	Aligie DHA, deg	Coordinates of atoms A
			I		
O(1)–H(1) O(3)	0.81(8)	1.74(8)	2.529(8)	165(8)	<i>x</i> , <i>y</i> , <i>z</i>
O(4)-H(4) O(2)	0.63(7)	1.89(7)	2.505(9)	169(9)	<i>x</i> , <i>y</i> , <i>z</i>
N(5) - H(5A) - F(3)	0.86	2.17	3.00(3)	163	x, y - 1, z
$N(5)-H(5B)\cdots O(1w)$	0.86	1.99	2.83(3)	166	<i>x</i> , <i>y</i> , <i>z</i>
N(6) - H(6A) - F(1)	0.86	1.98	2.84(3)	177	-x, -y + 1, -z + 1
N(6) - H(6A) - O(4)	0.86	2.27	2.93(1)	134	x - 1, y, z
N(5A) - H(5A) - F(2A)	0.86	2.03	2.73(4)	138	-x + 1, -y + 1, -z + 1
N(6A)-H(6A)F(5A)	0.86	1.93	2.72(4)	152	-x + 1, -y + 1, -z + 1
N(7) - H(7) - O(2w)	0.86	2.01	2.86(3)	170	-x, -y + 1, -z + 2
N(7) - H(7A) - F(4A)	0.86	2.13	2.92(2)	153	-x, -y + 1, -z + 2
N(7) - H(7B) - O(3)	0.86	2.04	2.893(9)	174	<i>x</i> , <i>y</i> , <i>z</i>
N(8)–H(8A) F(6A)	0.86	1.99	2.77(3)	150	x, y - 1, z + 1
N(8) - H(8A) - F(2)	0.86	2.10	2.87(3)	148	-x, -y + 1, -z + 2
N(8)–H(8A) O(2)	0.86	2.06	2.890(8)	162	-x+1, -y, -z+2
			II	1	I
O(1)–H(1) O(3)	0.82	1.73	2.516(11)	161	<i>x</i> , <i>y</i> , <i>z</i>
O(4)-H(4) O(2)	0.82	1.72	2.513(10)	161	<i>x</i> , <i>y</i> , <i>z</i>
N(5) - H(5A) - F(3A)	0.86	2.01	2.76(4)	145	x, y + 1, z - 1
N(5) - H(5A) - F(6A)	0.86	2.00	2.77(4)	150	-x + 1, -y + 2, -z + 1
N(5) - H(5A) - F(5)	0.86	2.26	2.95(2)	138	x, y + 1, z - 1
$N(5)-H(5B)\cdots O(4w)$	0.86	2.31	2.86(6)	122	<i>x</i> , <i>y</i> , <i>z</i>
$N(5)-H(5B)\cdots O(2w)$	0.86	2.60	3.24(2)	132	<i>x</i> , <i>y</i> , <i>z</i>
N(6) - H(6A) - F(3A)	0.86	1.88	2.64(4)	147	x, y + 1, z - 1
N(6) - H(6B) - F(2A)	0.86	1.81	2.58(4)	148	-x + 2, -y + 2, -z + 1
N(6) - H(6B) - F(2)	0.86	2.15	2.99(3)	167	-x + 2, -y + 2, -z + 1
N(7) - H(7A) - O(1w)	0.86	2.02	2.85(3)	163	<i>x</i> , <i>y</i> , <i>z</i>
N(7) - H(7A) - O(5w)	0.86	2.24	3.01(4)	149	<i>x</i> , <i>y</i> , <i>z</i>
N(7) - H(7B) - O(3)	0.86	1.99	2.85(1)	175	<i>x</i> , <i>y</i> , <i>z</i>
N(8) - H(8A) - O(5w)	0.86	2.25	3.02(4)	150	<i>x</i> , <i>y</i> , <i>z</i>
N(8) - H(8A) - F(5A)	0.86	2.34	2.93(3)	126	-x + 1, -y + 1, -z + 2
$N(8) - H(8A)^{}F(4)$	0.86	2.51	3.01(2)	118	<i>x</i> , <i>y</i> , <i>z</i>
N(8) - H(8B) - O(2)	0.86	2.10	2.93(1)	162	-x + 1, -v + 2, -z + 1

Table 3. Geometrical parameters of the intramolecular and intermolecular hydrogen bonds in structures I and II

occupies one axial position in complex I instead of the expected coordinated Seu molecule. It is known that Thio, Seu, and their derivatives form bis(dications) [33-38] and tris(dications) [39, 40]; for selenourea, the mechanisms for the formation of elemental selenium have been proposed [23, 41, 42]. Apart from elemental selenium, the final oxidation products of Seu are cyanamide and water [41]. Based on the literature data [41, 43], we believe that the formation of the

N(8)-H(8B)...O(2)

ligand Se-Seu involves addition of elemental selenium to Seu in the radical form as shown below:

-x + 1, -y + 2, -z + 1

$$\begin{array}{ccc} H_2N^+\\ H_2N\\ H_2N\\ Seu \end{array} \xrightarrow{} \begin{array}{c} H_2N\\ H_2N\\ Se-Seu \end{array} \xrightarrow{} \begin{array}{c} Se-Seu \end{array}$$

For both types of complex cations in structures I and II, the coordination polyhedron of the Co atom is

2.93(1)



Fig. 1. Structures of (a) the complex cations $[Co(DH)_2(Seu)_2]^+$ and $[Co(DH)_2(Seu)(Se-Seu)]^+$ in I and (b) $[Co(DH)_2(Seu)(Se-Seu)]^+$ in II.



Fig. 2. Fragment of the crystal structure with the cation (a) $[Co(DH)_2(Seu)_2]^+$ and (b) $[Co(DH)_2(Seu)(Se-Seu)]^+$ in I.

an octahedron made up of four N atoms of two DH⁻ residues in the equatorial plane and two axial Se atoms of Se-Seu and Seu molecules. The Co–N distances in structures I and II are 1.885(6)-1.890(6) and 1.868(8)-1.910(8) Å, respectively (Table 2), which agree with analogous distances in other Thio-containing Co(III) dioximates [20-22] and are somewhat shorter than those in NH₄[Co(DH)₂(SeCN)₂] [19]. Four coordinated N atoms of two ligands DH⁻ are

coplanar (±0.020 (I) and ±0.029 Å (II)), also with the metal atom (0.013 (I) and 0.022 Å (II)). The Co–Se distances in structures I and II (2.41(1)–2.49(3) Å in I and 2.422(2) and 2.428(2) Å in II) are appreciably longer than those in cobalt dimethylglyoximate with the SeCN anion (2.383 Å [19]). The monodeprotonated bidentate chelating anions DH⁻ form two intramolecular hydrogen bonds (IHBs) O(1)–H···O(3) and O(4)–H···O(2) (O...O 2, 2.529(8) and 2.505(9) Å



Fig. 3. Fragment of the crystal structure of complex II.

in I and 2.516(11) and 2.513(10) Å in II) (Table 3). Thus, apart from two five-membered chelate rings resulting from the coordination of DH⁻, the complexes contain two six-membered pseudochelate rings, which can be described by Graph S6. Various intramolecular interactions between the axial ligands Seu and Se-Seu and the equatorial fragment in the complex cations were determined (Fig. 1). In the cation $[Co(DH)_2(Seu)_2]^+$ of structure I, one coordinated Seu molecule is hydrogen-bonded to the oxime O atom. Similar IHBs stabilize the positions of the axial ligands Seu in the cation $[Co(DH)_2(Seu)(Se-Seu)]^+$. The donor-acceptor distances in the IHB N(7)-H···O(3) are 2.893(9) and 2.85(1) Å in structures I and II, respectively. The dihedral angles between the planes Se(2)C(10)N(7)N(8) and N(1)N(2)N(3)N(4) in I and II are 74.4° and 105.5°, respectively. The fragment Se(1)C(9)N(5)N(6) in structure I makes with this plane a dihedral angle of 19.1°. Such a position of the second Seu molecule is probably due to a $\pi \cdots \pi$ interaction between this molecule and the chelate ring Co(1)N(1)N(2)C(1)C(3) (the distance between their mean-square planes is 2.977 Å). In the complex cations $[Co(DH)_2(Seu)(Se-Seu)]^+$, the position of the ligand Se-Seu seems to be stabilized by the intramolecular interaction Se $\cdots \pi$. The Se(1*B*) \cdots X distance is 3.190 and 3.251 Å in structures I and II, respectively of (X is the center the chelate ring Co(1)N(1)N(2)C(1)C(3)). The Se–Se bond lengths in Se-Seu (2.19(3) (I) and 2.282(2) Å (II)) are shorter than those in the organic dication $((Seu)_2^{2+} (2.38(1) \text{ Å}))$

[43]). The angles SeSeC $(91(2)^{\circ}$ (I) and $100.9(8)^{\circ}$ (II)) are close to the corresponding angles in the dications [36, 37, 43].

The Ti–F and Zr–F bond lengths in the octahedral anions $[TiF_6]^{2-}$ in I and $[ZrF_6]^{2-}$ in II are 1.73(2)–1.97(3) and 1.96(2)–2.03(2) Å, respectively. These values do not differ from those found in Co(III) dioximates with the same anions [25, 44].

In the crystal packing of complexes I and II, the organizing role is played by outer-sphere anions stabilizing the positions of the coordinated selenourea molecules in the complex cations. All F atoms of the anions $[TiF_6]^{2-}$ and $[ZrF_6]^{2-}$ act as proton acceptors in a system of intermolecular hydrogen bonds N–H···F and O(w)–H···F (Figs. 2a, 2b, 3; Table 3). As a result, the second coordination spheres of the Ti and Zr atoms contain four complex cations and four water molecules. The complex cations in structures I and II are united into chains through the intermolecular hydrogen bonds N–H···O with the amino groups of the coordinated Seu and Se-Seu molecules as proton donors and with the oxime O atoms as proton acceptors (Table 3).

REFERENCES

- 1. Chakravorty, A., Coord. Chem. Rev., 1974, vol. 13, no. 1, p. 1.
- 2. Bresciani-Pahor, N., Farcolin, M., Marzilli, L.G., et al., *Coord. Chem. Rev.*, 1985, vol. 63, no. 4, p. 1.
- Randaccio, L., Bresciani-Pahor, N., Zangrando, E., and Marzilli, L.G., *Chem. Soc. Rev.*, 1989, vol. 18, p. 225.
- 4. De Ridder, D.J.A., Zangrando, E., and Burgi, H.-B., *J. Mol. Struct.*, 1996, vol. 374, nos. 1-3, p. 63.
- 5. Rogachev, B.G. and Khidekel', M.L., *Izv. Akad. Nauk* SSSR, Ser. Khim., 1969, no. 1, p. 141.
- 6. Proskina, N.N., Shafranskii, V.N., and Ablov, A.V., *Izv. Akad. Nauk MSSR*, 1968, no. 6, p. 7.
- Desyatnik, A.A., Gerbeleu, N.V., Coropceanu, E.B., et al., *Koord. Khim.*, 2002, vol. 28, no. 2, p. 144 [*Russ. J. Coord. Chem.* (Engl. Transl.), vol. 28, no. 2, p. 135].
- Coropceanu, E., Bologa, O., Deseatnic, A., et al., *Bul. Inst. Polit. Iasi*, 2003, vol. 59, no. Fasc. 5, p. 293.
- Bourosh, P.N., Coropceanu, E.B., Desyatnik, A.A., et al., *Koord. Khim.*, 2009, vol. 35, no. 10, p. 761 [*Russ. J. Coord. Chem.* (Engl. Transl.), vol. 35, no. 10, p. 751].
- Deseatnic, A., Stratan, M., Coropceanu, E., et al., Patent MD, *BOPI*, 2009, no. 7.
- 11. Garbalau, N., Simonov, Yu., Deseatnic, A., et al., Patent MD 1203, *BOPI*, 1999, no. 4, p. 32.
- Garbalau, N., Simonov, Yu., Bouros, P., et al., Patent MD 2833, *BOPI*, 2005, no. 8, p. 31.
- 13. Badiello, R, in *The Chemistry of Organic Selenium and Tellurium Compounds*, Patai, S. and Rappoport, Z.N.Y., Eds., New York: Wiley, 1986, p. 287.
- 14. Sieber, F., Daziano, J., Gunther, W.H., et al., *Phosphorus, Sulfur Silicon Relat. Elem.*, 2005, vol. 180, p. 647.

- 15. Zhang, J.S., Gao, X.Y., Zhang, L.D., and Bao, Y.P., *Biofactors*, 2001, vol. 15, p. 27.
- 16. Zhang, J., Wang, H., Bao, Y., and Zhang, L., *Life Sci.*, 2004, vol. 75, p. 237.
- 17. Huang, B., Zhang, J., Hou, J., and Chen, C., *Free Radicals Biol. Med.*, 2003, vol. 35, p. 805.
- Allen, F.H., Acta Crystallogr., Sect. B: Struct. Sci., 2002, vol. 58, nos. 3–4, p. 380.
- Samus', I.D. and Belov, N.V., *Dokl. Akad. Nauk SSSR*, 1970, vol. 193, no. 2, p. 333.
- Bourosh, P.N., Coropceanu, E.B., Simonov, Yu.A., et al., *Zh. Neorg. Khim.*, 2002, vol. 47, no. 10, p. 1604 [*Russ. J. Inorg. Chem.* (Engl. Transl.), vol. 47, no. 10, p. 1467].
- Bourosh, P.N., Coropceanu, E.B., Simonov, Yu.A., et al., *Koord. Khim.*, 2002, vol. 28, no. 9, p. 689 [*Russ. J. Coord. Chem.* (Engl. Transl.), vol. 28, no. 9, p. 647].
- Bourosh, P.N., Coropceanu, E.B., Bologa, O.A., et al., *Koord. Khim.*, 2004, vol. 30, no. 6, p. 403 [*Russ. J. Coord. Chem.* (Engl. Transl.), vol. 30, no. 6, p. 375].
- 23. Priyadarsini, K.I., Mishra, B., Maity, D.K., and Mohan, H., *Phosphorus, Sulfur Silicon Relat. Elem*, 2005, vol. 180, no. 3, p. 985.
- 24. Sheldrick, G.M., Acta Crystallogr., Sect. A: Found. Crystallogr., 2008, vol. 64, p. 112.
- 25. Rija, A.P., Coropceanu, E.B., Bologa, O.A., et al., *Zh. Strukt. Khim.*, 2007, vol. 48, no. 6, p. 1197.
- 26. Bellamy, L.J., *The Infra-Red Spectra of Complex Molecules*, London: Methuen, 1959.
- 27. Kharitonov, Yu.Ya., Brega, V.D., and Ablov, A.V., *Zh. Neorg. Khim.*, 1970, vol. 15, no. 11, p. 3162.
- 28. Aitken, G.B., Duncan, J.L., and McQuillan, G.P., J. Chem. Soc., Dalton Trans., 1972, p. 2103.
- 29. Gulya, A.P., *Doctoral Sci. (Chem.) Dissertation*, Moscow: Institute of General and Inorganic Chemistry, 1989.

- Gulya, A.P., Ablov, A.V, Bologa, O.A., and Shcherbakov, V.A., *Koord. Khim.*, 1976, vol. 2, no. 1, p. 14.
- 31. Popa, I.A., Shafranskii, V.N., and Gulya, A.P., *Koord. Khim.*, 1988, vol. 14, no. 4, p. 483.
- 32. Kinoshita, S. and Masuda, I., *Polyhedron*, 1985, vol. 4, no. 7, p. 1245.
- 33. Lis, T., Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem., 1980, vol. 36, p. 2782.
- Villa, A.C., Manfredotti, A.G., Nardelli, M., and Tani, M.E.V., Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem., 1972, vol. 28, p. 356.
- 35. Bombicz, P., Mutikainen, I., Krunks, M., et al., *Inorg. Chim. Acta*, 2004, vol. 357, p. 513.
- Villa, A.C., Nardelli, M., and Tani, M.E.V., Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem., 1970, vol. 26, p. 1504.
- 37. Pathirana, H.M.K.K., Reibenspies, J.H., Meyers, E.A., and Zingaro, R.A., *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1991, vol. 47, p. 903.
- 38. Bierbach, U., Saak, W., Haase, D., and Pohl, S., *Z. Naturforsch., B: Chem. Sci.*, 1990, vol. 45, p. 45.
- 39. Hauge, S., Opedal, D., and Arskog, J., *Acta Chem. Scand. A*, 1975, vol. 29, p. 225.
- 40. Hauge, S., Acta Chem. Scand. A, 1979, vol. 33, p. 317.
- 41. Mishra, B., Hassan, P.A., Priyadarsini, K.I., and Mohan, H., J. Phys. Chem. B, 2005, vol. 109, p. 12718.
- 42. Mishra, B., Priyadarsini, K.I., Mohan, H., and Hassan, P.A., *The National Symp. Radiation & Photochemistry*, Dharwad (India): Univ. of Karnataka, 2005.
- 43. Chiesi, A., Grossoni, G., Nardelli, M., and Vidoni, M.E., *Chem. Commun.*, 1969, p. 404.
- 44. Rija, A., Bourosh, P., Coropceanu, E., et al., *Mold. J. Phys. Sci*, 2010, vol. 9, no. 2, p. 162.