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Sulfanylamide-containing Coordination Compounds of 3*d*-Elements with 2,4-Pentanedione Bis-thiosemicarbazone and Bis-4-phenylthiosemicarbazone

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Abstract—Thiosemicarbazide and 4-phenylthiosemicarbazide react in ethanol with 2,4-pentanedione in the presence of manganese, cobalt, nickel, copper, and zinc acetates hydrates and streptamin (Sf^1), sulfaethidole (Sf^2), and sulfadimidine (Sf^3) to form coordination compounds of the composition $M(Sf^{1-3})(L^{1-2}) \cdot nH_2O$ (M = Mn, Co, Ni, Cu, Zn; H_2L^1 is 2,4-pentanedione bis-thiosemicarbazone, H_2L^2 is 2,4-pentanedione bis-4-phenylthiosemicarbazone; n = 0–6). All the complexes synthesized are monomeric. Thiosemicarbazones (H_2L^1 and H_2L^2) behave as twice deprotonated S,N,N,S-tetradentate ligands, while sulfanylamides (Sf^{1-3}) act as monodentate ones. Thermolysis of these substances proceeds through the stages of dehydration (65–95°C) and complete thermal decomposition (430–560°C). It is found that the complex $[Cu(Sf^2)(L^1)] \cdot 4H_2O$ in the concentration 10^{-5} M inhibits the growth and fission of 100% cancer cells of the human myeloid leukemia (HL-60).

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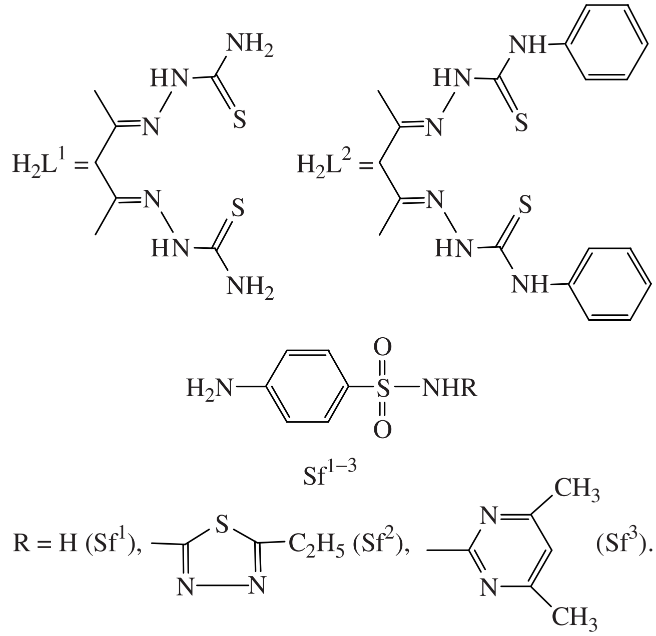
Thiosemicarbazide [H_2N–NH–C(S)–NH_2] derivatives are widely used in medicine for treating various diseases [1–3]. All of them possess a broad set of donor atoms and may react with metal ions to form coordination compounds of varied structure and composition [4–6]. It is established [7–9] that in many cases the biological activity of the above-mentioned drugs correlates with their ability to complex formation. Therefore the accumulation of experimental data concerning synthesis and physicochemical investigation of thiosemicarbazide derivatives composition and structure presents scientific as well as practical interest.

The aim of this work is the evaluation of optimal synthetic conditions for preparing mixed-ligand coordination compounds of manganese, cobalt, nickel, copper, and zinc with 2,4-pentanedione bis-thiosemicarbazone (H_2L^1) and bis-4-phenylthiosemicarbazone (H_2L^2) incorporating sulfanylamides (Sf^{1-3}) like streptamin (Sf^1), sulfaethidole (Sf^2), and sulfadimidine (Sf^3), and investigation of their properties.

The experiment showed that when hot (50–55°C) ethanolic solutions of acetates of the above-mentioned



metals are reacted with 2,4-pentanedione, thiosemicarbazide or 4-phenylthiosemicarbazide and sulfanylamides (Sf^{1-3}) taken in the 1 : 1 : 2 : 2 molar ratio fine crystalline substances **I–XXX** are formed. On the basis of the elemental analysis data (Table 1) the composition $M(Sf^{1-3})(L^{1,2}) \cdot nH_2O$ was assumed [M = Mn (**I–III, XVI–XVIII**), Co (**IV–VI, XIX–XXI**), Ni

Table 1. Physicochemical characteristics of the sulfanylamide-containing coordination compounds of 3*d* elements with 2,4-pentanedione, bis-thiosemicarbazone, and bis-phenylthiosemicarbazone.

Comp. no.	Yield, %	μ_{eff},[a] BM	æ,[a] Ω^{-1} cm^2 mol^{-1}	Found, %			Formula	Calculated, %		
				M[b]	N	S		M[b]	N	S
I	70	5.83	4	7.65	19.94	18.09	$C_{19}H_{34}MnN_{10}O_7S_4$	7.89	20.09	18.36
II	75	5.94	2	5.85	21.46	20.99	$C_{27}H_{40}MnN_{14}O_6S_6$	6.09	21.71	21.26
III	74	5.80	5	5.78	21.29	14.27	$C_{31}H_{46}MnN_{14}O_7S_4$	6.05	21.56	14.08
IV	64	4.95	3	8.40	20.22	18.53	$C_{19}H_{32}CoN_{10}O_6S_4$	8.64	20.50	18.74
V	72	4.99	2	5.78	19.75	19.35	$C_{27}H_{48}CoN_{14}O_{10}S_6$	6.03	20.02	19.61
VI	68	5.03	2	6.30	22.04	14.07	$C_{31}H_{44}CoN_{14}O_6S_4$	6.59	21.90	14.30
VII	66	2.87	5	8.85	21.47	19.50	$C_{19}H_{28}N_{10}NiO_4S_4$	9.12	21.64	19.78
VIII	75	3.16	2	6.40	21.77	21.31	$C_{27}H_{38}N_{14}NiO_5S_6$	6.64	22.05	21.60
IX	72	2.96	6	6.60	22.71	14.66	$C_{31}H_{40}N_{14}NiO_4S_4$	6.87	22.82	14.90
X	64	1.87	3	9.29	21.06	18.84	$C_{19}H_{30}CuN_{10}O_5S_4$	9.56	20.90	19.10
XI	69	2.12	3	6.47	20.41	19.97	$C_{27}H_{44}CuN_{14}O_8S_6$	6.75	20.68	20.25
XII	71	1.96	4	6.55	20.69	13.45	$C_{31}H_{48}CuN_{14}O_8S_4$	6.84	20.94	13.68
XIII	66	[c]	3	10.16	21.19	19.48	$C_{19}H_{28}N_{10}O_4S_4Zn$	9.95	21.44	19.60
XIV	67	[c]	6	7.11	20.79	20.38	$C_{27}H_{42}N_{14}O_7S_6Zn$	6.98	21.05	20.62
XV	69	[c]	3	7.28	22.40	14.57	$C_{31}H_{40}N_{14}O_4S_4Zn$	7.51	22.66	14.80
XVI	62	5.97	4	6.19	16.23	14.81	$C_{31}H_{42}MnN_{10}O_7S_4$	6.48	16.49	15.08
XVII	60	5.85	2	4.57	17.10	16.81	$C_{39}H_{56}MnN_{14}O_{10}S_6$	4.88	17.39	17.04
XVIII	73	5.91	6	5.01	18.63	18.54	$C_{39}H_{52}MnN_{14}O_6S_6$	5.27	18.79	18.41
XIX	70	5.14	4	7.11	16.17	14.76	$C_{31}H_{42}CoN_{10}O_7S_4$	6.92	16.41	15.01
XX	71	5.01	3	5.30	18.24	17.75	$C_{39}H_{48}CoN_{14}O_6S_6$	5.57	18.51	18.13
XXI	72	5.06	2	7.07	18.47	18.07	$C_{39}H_{52}CoN_{14}O_6S_6$	6.92	18.72	18.34
XXII	71	2.85	3	7.04	16.27	14.76	$C_{31}H_{42}N_{10}NiO_7S_4$	6.92	16.41	15.01
XXIII	70	2.96	4	4.97	17.09	17.11	$C_{39}H_{56}N_{14}NiO_{10}S_6$	5.22	17.33	16.98
XXIV	73	3.04	3	5.34	18.36	11.99	$C_{43}H_{52}N_{14}NiO_6S_4$	5.64	18.72	12.23
XXV	65	1.79	4	6.75	15.09	13.79	$C_{31}H_{48}CuN_{10}O_{10}S_4$	7.02	15.35	14.04
XXVI	66	1.75	3	5.47	17.25	16.89	$C_{39}H_{54}CuN_{14}O_9S_6$	5.72	17.53	17.17
XXVII	70	1.79	4	5.60	17.74	11.48	$C_{43}H_{56}CuN_{14}O_8S_4$	5.88	18.01	11.76
XXVIII	65	[c]	2	7.17	16.19	14.33	$C_{31}H_{44}N_{10}O_8S_4Zn$	7.41	15.96	14.60
XXIX	69	[c]	2	5.71	17.51	17.14	$C_{39}H_{52}N_{14}O_8S_6Zn$	5.90	17.80	17.43
XXX	72	[c]	3	5.79	18.03	11.71	$C_{43}H_{54}N_{14}O_7S_4Zn$	6.07	18.30	11.95

[a] at 294 K. [b] M is metal. [c] Diamagnetic complex.

(**VII–IX, XXII–XXIV**), Cu (**X–XII, XXV–XXVII**), Zn (**XIII–XV, XXVIII–XXX**); Sf^{1-3} = Sf^1(**I, IV, VII, X, XIII, XVI, XIX, XXII, XXV, XVIII**), Sf^2 (**II, V, VIII, XI, XIV, XVII, XX, XXIII, XXVI, XXIX**), Sf^3 (**III, VI, IX, XII, XV, XVIII, XXI, XXIV, XXVII, XXX**); H_2L^{1-2} = H_2L^1 (**I–XV**), H_2L^2 (**XVI–XXX**); *n* = 0 (**VIII, IX, XIII, XV**), 1 (**VIII, X**), 2 (**II, IV, VI, XVIII.XX, XXI, XXIV**), 3 (**I, III, XIV, XVI, XIX, XXII, XXX**), 4 (**XI, XII, XXVIII–XXIX**), 5 (**XXVI**), 6 (**V, XVII, XXIII, XXV**)].

The coordination compounds obtained **I–XXX** are insoluble in ether, poorly soluble in water and alcohols, and well soluble in DMF, DMSO, and acetonitrile. Their yields and physicochemical characteristics are presented in Table 1.

On the basis of the elemental analysis data of the complexes **I–XXX** (Table 1) it can be suggested that similarly to the process reported in [10] the condensation of 2,4-pentanedione with thiosemicarbazide and 4-phenylthiosemicarbazide takes place in the reaction mixture on the martix of the metal ions under investigation. The Schiff bases formed (H_2L^1 and H_2L^2) react with manganese, cobalt, nickel, copper, and zinc acetates in the presence of sulfanyl amides (Sf^{1-3}) to give the mixed-ligand coordination compounds **I–XXX**. Evaluation of molar electroconductivity of the compounds obtained in DMF showed that all of them are nonelectrolytes (æ 2–6 Ω^{-1} cm^2 mol^{-1}).

In order to establish the manner of coordination of the ligands (H_2L and Sf^{1-3}) to the central ions comparative analysis of the IR spectra of the complexes obtained **I–XXX**, of starting thiosemicarbazides and sulfanylamides (Sf^{1-3}), and also of the coordination compounds of the transition metals with the analogous Schiff bases published in [4–6, 10] was carried out. It was found (Table 2) that in compounds under study thiosemicarbazones H_2L^{1-2} behave as tetradentate twice deprotonated S,N,N,S-ligands and add to the complex-forming ions through the sulfur and the azomethine nitrogen atoms to form either one six-membered metallocycle or two five-membered ones. It is confirmed by disappearance of the ν(NH) and ν(C=S) absorption bands in the IR spectra of complexes under study. In the IR spectra of free semicarbazides these bands are observed at 1545–1535 and 1135–1115 cm^{-1} respectively. Besides, in the spectra of complexes the ν(C–S) absorption band appears at 755–735 cm^{-1}, and the ν(C=N) band is splitted to two components and shifted by 20–25cm^{-1} to the low frequency side as compared to the free thiosemicarbazones. In the IR spectra of complexes an absorption band at 1570–1560 cm^{-1} is present. According to the published data [4, 5, 10] it is attributed to the >C=N–N=C< bonds vibrations. Such character of spectra indicates that in the course of formation of the coordination compounds **I–XXX** the thiosemicarbazones undergo enolization. Participation of the other functional groups of thiosemicarbazones H_2L^{1-2} in the coordination with the central atom is excluded because their characteristic absorption bands are revealed in the same regions as in spectra of free thiosemicarbazides, 2,4-pentanedione, and the analogous azomethines. Presence of sulfanylamides in the compounds under study is confirmed by the corresponding characteristic absorption bands. It follows from the data obtained that streptamin is coordinated through the nitrogen atom of one amino group, while sulfaethiodole is coordinated by the thiadiazole nitrogen atom, and sulfadimidine by one of the pyrimidine atoms. The above-mentioned way of coordination of the ligands is confirmed by the fact that in the spectra of complexes **I–XXX** a series of new absorption bands appears in the range 530–405 cm^{-1}. According to the published data they correspond to the metal-nitrogen (530–505 cm^{-1}), metal-oxygen (495–485 cm^{-1}) and metal-sulfur (480–479 cm^{-1}) bond vibrations.

Magnetochemical studies of complexes **I–XII, XVI–XXVII** at room temperature (294 K) showed (Table 1) that the values of the effective magnetic moments of compounds **I–III, XVI–XVIII** vary within the limits 5.80–5.97 BM indicating the presence of the manganese(II) ions in the high-spin state. The cobalt and nickel complexes **IV–IX**, **XVI–XVIII** are paramagnetic. Their magnetochemical characteristics show that their central atoms have the pseudo-octahedral ligand surrounding ($t_{2g}^5e_g^2$ and $t_{2g}^6e_g^2$ electronic states respectively). For the copper compounds **X–XII, XXV–XXVII** the values of the effective magnetic moments correspond to the spin values of one unpaired electron. These experimental data permit to suggest that such complexes are monomeric.

On the basis of thermogravimetric analysis of the compounds synthesized **I–XXX** it was established (Table 3) that their thermolysis proceeds in two stages. The DTA curve of the majority of complexes exhibits an endothermic effect at 70–95°C. Its comparatively low temperature permits to state that dehydration of the studied compounds occurs. Subsequent thermo-

Table 2. The absorption band frequencies in the IR spectra of the sulfanylamide-containing coordination compounds of 3*d*-elements with 2,4-pentanedione, bis-thiosemicarbazone, and bis-4-phehylthiosemicarbazone

Comp. no.[a]	ν(NH_2) ν(NH)	ν(C=N)	ν(>C=N–N=C<)	$ν_{as}(SO_2)$ $ν_2(SO_2)$	δ(C–N)	ν(C=S)	ν(C–N)	ν(S–N)	ν(C–S)	δ(SO_2)	ν(M–N)[b] ν(M–O) ν(M–S)
Thio- semi- carbazone	3363, 3261 3172, 1531	–	–	–	1376 1112	800	975 935	–	–	–	–
Sf[1]	3440, 3330 3210, 1530	–	–	1320 1145	1330 1115	–	975 930	860	745	560	–
I	3420, 3340 3190, 3175, 1520	1595	1570	1325 1145	1370 1340 1115	–	970 940	855	740 730	560	525, 480, 460, 430
IV	3425, 3335, 3200, 3170, 1515	1600	1575	1325 1145	1375 1335 1115	–	970 930	850	745 730	555	515, 490, 475, 415
X	3420, 3335, 3200, 3175, 1520	1600	1570	1320 1145	1375 1330 1115	–	970 930	855	745 735	560	520, 485, 470, 420
Sf[2]	3435, 3330 3200, 1535	1620		1320 1135	1330 1120	–	985 930	870	750	560	–
II	3430, 3325, 3195, 3175, 1530	1615 1600 1590	1565	1325 1140	1370 1335 1125	–	980 935	865	745 730	555	525, 480, 465, 425
V	3430, 3335, 3200, 3175, 1530	1615 1595 1590	1570	1320 1140	1375 1335 1120	–	980 930	865	745 735	560	530, 485, 470, 420
Sf[3]	3460, 3350 3245, 1535	1630	–	1320 1145	1335 1110	–	980 940	870	755	570	–
III	3455, 3355, 3250, 3170, 1530	1610 1600 1590	1570	1325 1140	1370 1330 1110	–	975 935	865	745 730	560	525, 490, 475, 430
VI	3450,3355, 3245, 3175, 1530	1615 1605 1590	1570	1320 1140	1375 1335 1110	–	975 940	865	750 735	565	530, 480, 470, 425
XX	3445, 3340, 3245, 3160, 1525	1610 1595 1590	1560	1320 1130	1360 1325 1100	–	970 930	855	740 725	540	510, 475, 455, 410
XXVI	3440, 3345, 3240, 3160, 1520	1610 1600 1590	1565	1325 1140	1360 1330 1100	–	970 935	855	735 730	545	520, 475, 460, 425
XXIX	3440, 3345, 3245, 3165, 1525	1605 1600 1595	1570	1330 1135	1365 1315 1105	–	965 935	860	735 725	540	530, 480, 465, 425

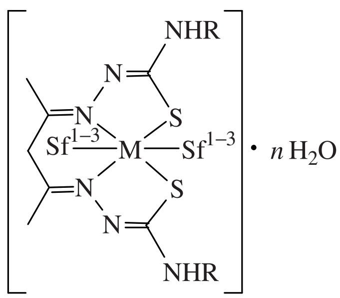
[a] The complexes were preliminary maintained in a drying cabinet at 105°C till constant mass. [b] M is metal.

Table 3. Results of thermogravimetric analysis of the sulfanylamide-containing coordination compounds of 3*d*-elements with 2,4-pentanedione, bis-thiosemicarbazone, and bis-4-phenylthiosemicarbazone

Comp. no.	Temperature of the maximum point of the first endoeffect on the DTA curve, °C	Weight loss			Kinetic parameters		Temperature of complete decomposition, °C
		found, %	calculated, %	liberating	E_a, kJ mol^{-1}	log Z	
I	70	7.5	7.7	3 H_2O	35.6	3.6	560
II	75	4.3	4.0	2 H_2O	38.2	3.9	540
III	90	6.0	5.9	3 H_2O	41.6	4.2	530
IV	75	5.0	5.3	2 H_2O	36.2	3.8	535
V	85	11.5	11.7	6 H_2O	37.2	3.9	530
VI	90	4.3	4.0	2 H_2O	38.0	3.9	510
VII	–	–	–	–	–	–	530
VIII	80	2.3	2.0	H_2O	39.1	4.0	510
IX	–	–	–	–	–	–	510
X	70	2.5	2.7	H_2O	32.8	3.4	480
XI	85	7.5	7.6	4 H_2O	36.8	3.7	460
XII	80	7.5	7.7	4 H_2O	36.0	3.7	445
XIII	–	–	–	–	–	–	470
XIV	75	5.5	5.8	3 H_2O			460
XV	–	–	–	–	–	–	440
XVI	75	6.5	6.4	3 H_2O	33.1	3.4	530
XVII	90	9.5	9.6	6 H_2O	39.2	4.0	520
XVIII	95	3.2	3.5	2 H_2O	41.4	4.2	500
XIX	85	6.5	6.3	3 H_2O	37.6	3.9	500
XX	80	4.0	3.6	2 H_2O	36.1	3.7	470
XXI	85	3.5	3.4	2 H_2O	35.5	3.6	460
XXII	70	6.5	6.3	3 H_2O	32.9	3.4	480
XXIII	75	9.2	9.5	6 H_2O	35.8	3.7	470
XXIV	70	3.5	3.4	2 H_2O	32.4	3.4	445
XXV	70	12.0	11.8	6 H_2O	37.5	3.9	450
XXVI	75	8.0	8.1	5 H_2O	34.2	3.5	440
XXVII	85	6.5	6.6	4 H_2O	36.4	3.7	425
XXVIII	80	8.5	8.2	4 H_2O	35.0	3.6	450
XXIX	75	6.8	6.5	4 H_2O	32.9	3.4	440
XXX	70	4.7	5.0	3 H_2O	31.6	3.2	430

effect on the DTA curve of complexes under investigation is observed at 430–560°C. It is exothermic and is connected with the thermooxidative destruction of the coordinated sulfanylamides Sf^{1-3} and thiosemicarbazones H_2L^1, H_2L^2. It is found that the temperature (*t*) of complete decomposition of substance depends on the nature of the central atom and the inner sphere ligands. When the composition of the coordination compounds is similar it varies as follows: t(Co) > t(Ni) > t(Mn) > t(Cu) > t(Zn); $t(H_2L^1)$ > $t(H_2L^2)$; $t(Sf^1$ > $t(Sf^3)$ > $t(Sf^3)$. By means of the Horowitz-Metzger method [11] and considering Topor [12] supplement kinetic parameters of dehydration of the complexes under study were evaluated. The results obtained are presented in Table 3. It follows from these data that the activation energy (E_a) and the preexponential factor are close to kinetic parameters of similar reactions described in [13–15].

The above-presented physicochemical data permit to show the distribution of chemical bonds in the coordination compounds **I–XXX** by the following scheme.



M = Mn, Co, Ni, Cu, Zn; R = H, C_6H_5; Sf^1 – streptamin, Sf^2 – sulfaethiodole, Sf^3 – sulfadimidine; n = 0–6.

It was established [16–18] that many among coordination compounds of 3d-elements with thiosemicarbaside-based ligands selectively inhibit the growth of tumors. In this connection the anticancer activity of the complex **XI** was studied in vitro on the cells of human myeloid leukemia HL-60. It was found that the compound under study inhibits the growth of this type of cells exhibiting the activity similar to that of chemotherapeutic drugs used in medicine for the prophylaxis and treatment of leucosis. In the concentration 10^{-5} M this complex inhibits the growth and multiplication of 100% of the cancer cells. In the concentration 10^{-6} M no activity was observed.

EXPERIMENTAL

Resistance of the DMF solutions of complexes **I–XXX** (20°C, c 0.001 M) was measured by an R-38 rheochordic bridge. The IR spectra of substances after keeping in a drying cabinet at 105°C till the constant mass were registered on a Specord M-80 spectrometer from mulls in mineral oil. The effective magnetic moments of compounds **I–XII, XVI–XVII** were evaluated by Goui method. The molar magnetic susceptibility was calculated with the correction considering the dia-magnetic increment proceeding from the theoretical values of susceptibility of organic compounds. The derivatograms of complexes **I–XXX** were obtained on a Paulik–Paulik–Erdey derivatograph in a corundum crucible in the temperature range 20-1000°C in air using Al_2O_3 as reference.

The anticancer activity of the complex **XI** was studied "in vitro" using the cells of the HL-60 human myeloid leukemia by the standard procedure described in [19].

[2,4-Pentandione-bis(thiosemicarbazonato)]-bis (4-aminobenzenesulfamide)manganese trihydrate (I). To a hot (50–55°C) solution of 5 mmol of manganese(II) acetate tetrahydrate in 20 ml of ethanol 30 ml of the ethanol solution containing 5 mmol of 2,4-pentanedione and 10 mmol of thiosemicarbazide was added, and after 15–20 min of stirring 10 mmol of 4-aminobenzenesulfamide (streptamin) was added. The mixture obtained was heated with stirring for 50–60 min at 50–55°C. After cooling the dark brown precipitate was obtained. It was filtered off on a glass frit, washed with small amount of ethanol, and then with ether, and dried in air till the constant mass.

Compounds **II–XV** were prepared analogously from cobalt, nickel, copper, and zinc acetate hydrates, 2,4-pentanedione, thiosemicarbazide, and 4-aminobenzenesulfamide (streptamin), 2-(4-aminobenzenesulfamido)-5-ethyl-1,3,4-thiadiazole (sulfaethiodole), and 2-(4-aminobenzenesulfamido)-2,6-dimethylpyrimidine (sulfadimidine).

Complexes **XVI–XXX** were synthesized by analogous procedure from the above-mentioned salts, 2,4-pentanedione, 4-phenylthiosemicarbazide, and sulfanylamides Sf^{1-3} taken in the 1:1:2:2 molar ratio. The yields of the compounds **I–XXX** synthesized and some of their physicochemical characteristics are listed in Tables 1, 2.

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