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Coordination Compounds of 3*d* Metals Malonates and Glutarates with Thiosemicarbazide

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Abstract—Complexes of copper(II), nickel(II), and cobalt(III) malonates and glutarates with thiosemicarbazide have been prepared and studied by means of elemental analysis, IR spectroscopy, diffuse reflection spectroscopy, and thermogravimetry.

Keywords: thiosemicarbazide, malonate, glutarate, 3*d* metal, coordination compound

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Dicarboxylates are widely used as ligands to prepare various metal complexes applied in studies of electric conductivity, magnetism, *host–guest* compounds chemistry, ion exchange, catalysis, and nonlinear optics [1]. In particular, malonate ions are suitable for controlled assembly of complexes revealing unusual magnetic properties [2]. The structurally simple salts of malonic acid (H_2A) are suitable models to investigate the behavior of more complex biological objects. For example, metal malonates are known to inhibit metalloproteinases and can act as model of γ-carboxyglutamic acid [3].

Examples of dicarboxylates (malonate, oxalate, terephthalate, fumarate, succinate, adipate, etc) acting as bidentate chelating or bridging ligands have been described [4]. Despite the simple structure, malonate ion is relatively flexible. Compared to other dicarboxylates, malonate anion is notable for various types of coordination with metal ions in the crystal. Due to the 1,3-positioned carboxylic groups, malonate dianion may simultaneously act as bidentate chelating agent and bridging agent taking different conformations (*syn-syn*, *anti-anti*, and *syn-anti*) thus becoming a bi-, tri-, tetra-, penta-, or hexadentate ligand. Furthermore, oxygen atoms of malonate ion can form hydrogen bonds in the solid state, and the malonate-based structures can be three-dimensional, two-dimensional, or zigzag. The structural diversity of metal malonates is reflected in their magnetic properties [5].

Composition of the products of 3*d* metal ions interaction with malonate ion is highly dependent on the reaction conditions. For instance, in the case of copper(II) complexes containing exclusively malonate ions and water molecules, 6 crystal structures are known, most of them being dimeric or polymeric [6].

Previously we reported on preparation and studies of 3*d* metal complexes with thiosemicarbazide and various carboxylate ions [7–13]. In this work we extended those results with data on coordination compounds of copper(II), nickel(II), and cobalt(III) malonates with thiosemicarbazide (HL). For comparison, similar complexes were prepared with glutaric acid (H_2G) anion instead of malonate. Glutaric acid is one of malonate homologues containing odd number of carbon atoms.

The complexes were prepared via interaction of thiosemicarbazide aqueous solution with solid metal malonate or metal glutarate, the metal to thiosemicarbazide ratio being of 1 : 2. The metal salts were in turn formed by addition of the corresponding metal chloride to sodium malonate or glutarate. The prepared salts composition was of $M(A)\cdot 2H_2O$ (M = Ni or Co), $M(G)\cdot 3H_2O$ (M = Cu, Ni, or Co), and $Na_2[Cu(A)_2]\cdot 2H_2O$ (the latter being confirmed by X-ray diffraction analysis); the listed compositions were in line with those reported elsewhere [14].

Elemental analysis of the complexes (Table 1) revealed that the metal to thiosemicarbazide ratio was of 1 : 1 in the cases of nickel(II) malonate and copper(II) glutarate, 1 : 2 in the cases of copper(II) malonate and the both cobalt(III) salts, and 1 : 4 in the case of nickel(II) glutarate. In the case of the cobalt(II)

Table 1. Elemental analysis and appearance of compounds **I–VI**[a]

Comp. no.	Color	Found, %			Formula	Calculated, %		
		M	N	S		M	N	S
I	Violet	18.2	24.2	18.1	$C_5H_{12}CuN_6O_4S_2$ [Cu(HL)$_2$](A)	18.4	24.1	18.4
II	Pink	19.3	13.8	10.4	$C_{16}H_{50}N_{12}Ni_4O_{27}S_4$ [Ni(HL)$_2$]$_2$[Ni(A)$_2$(H$_2$O)$_2$]$_2$·7H$_2$O	19.6	13.9	10.6
III	Cherry	15.0	21.4	16.2	$C_5H_{17}CoN_6O_7S_2$ [Co(HL)L(A)]·3H$_2$O	14.9	21.2	16.2
IV	Gray	19.8	12.9	10.1	$C_6H_{15}CuN_3O_6S$ [CuL(H$_2$O)$_2$](HG)	19.9	13.1	10.0
V	Swamp green	10.3	30.8	23.2	$C_9H_{26}N_{12}NiO_4S_4$ [Ni(HL)$_4$(G)]	10.7	30.4	23.1
VI	Cherry	16.3	22.9	17.1	$C_7H_{15}CoN_6O_4S_2$ [Co(HL)L(G)]	15.9	22.7	17.3

[a] A, malonate ion; G, glutarate ion; HL, thiosemicarbazide.

complexes, the metal was oxidized into Co(III) by air oxygen, one of thiosemicarbazide being simultaneously deprotonated.

In the case of nickel(II) malonate the elemental composition corresponded to the Ni : HL : A ratio of 1 : 1 : 1; however, its structure was more complex. According to X-ray diffraction results, the nickel : thiosemicarbazide 1 : 2 complex was the cation in the product, whereas the nickel:malonate 1 : 2 complex acted as the anion (the anion was hydrated with two water molecules) [15]. Water molecules were found in the complexes of cobalt(III) malonate and copper(II) glutarate as well.

Hence, the inner sphere of cobalt complexes was the same in the cases of malonate and glutarate, whereas in the complexes of copper(II) and nickel(II) the inner sphere structure was dependent on the anion nature.

According to X-ray diffraction data [15], complex **II** was built of the $[Ni(HL)_2]^{2+}$ cations, the $[Ni(A)_2(H_2O)_2]^{2-}$ anions, and water of crystallization. Coordination polyhedron of nickel atom in the cation was slightly distorted *cis*-square; the HL ligands revealed bidentate chelate coordination with nickel via nitrogen and sulfur atoms to form the almost planar five-membered chelate ring. In the anion, malonate fragments showed bidentate chelate coordination to form the nonplanar six-membered ring; the central atom coordination was filled up to the octahedral one with pair of water molecules.

The IR spectral features of the free ligand and the studied complexes are summarized in Table 2. In all the cases but nickel(II) glutarate, formation of thiosemicarbazide complex resulted in weakening of thioamide I band, its frequency increasing; the effect was the most prominent in the cases of copper(II) complexes formation. In the spectrum of malonate complex **I** the thioamide I band appeared as shoulder of relatively strong $\nu_{as}(COO^-)$ band, whereas in the case of glutarate complex **IV** the thioamide I band was absent. In the spectrum of complex **V**, frequency of the thioamide I band was somewhat increased, and it was only slightly weaker than the $\nu_{as}(COO^-)$ band.

Thioamide II band in the spectrum of complex **V** differed from that in the spectra of other complexes as well. In particular, the thioamide II band was substantially weakened upon the complex **V** formation, the band frequency remaining unchanged; formation of other complexes resulted in the band shift towards higher frequency. In the spectra of malonate complexes of copper(II) and nickel(II), the thioamide II band overlapped with the $\nu_s(COO^-)$ band, therefore getting stronger. In particular, in the spectrum of complex **I** the thioamide II band was stronger that the $\delta(CH_2)$ band, whereas the bands intensity was reverse in the spectrum of starting copper(II) malonate. Thioamide III band was also weakened upon the complex formation; that band was weak in the spectrum of complex **VI**, being absent in the spectra of other complexes. The thioamide IV band was shifted towards lower frequency in the course of all the complexes formation. Basing on the above-listed observations and the previously published data [16] we suggested monodentate coordination of thiosemicarbazide via the sulfur atom in complex **V** and its bidentate coordination via the sulfur and nitrogen atoms in the other complexes.

Table 2. IR absorption bands (cm^{-1}) in the spectra of compounds **I–VI**, free thiosemicarbazide, and metal glutarates and malonates[a]

Compound	Thioamide bands				Absorption bands of water, ν(NH), and ν(NCS)	Absorption bands of anions	Absorption bands of COO^-
	I	II	III	IV			
HL	1530	1315	1000	800	3370, 3260, 3170 [ν(N−H)]		
$Na_2[Cu(A)_2]\cdot 2H_2O$					3350 [ν_{as}(O−H)], 3222 [ν_s(O−H)], 832 [$\rho_r(H_2O)$], 651 [$\tau(H_2O)$], 565 [$\rho_w(H_2O)$]	3037 [$\nu_{as}(CH_2)$], 2937 [$\nu_s(CH_2)$], 1438 [$\delta(CH_2)$], 1290 [$\rho_w(CH_2)$], 1185 [ν_{as}(C−C)], 990, 940 [ν_s(C−C)], 972 [$\rho(CH_2)$]	1592 [$\nu_{as}(COO^-)$], 1366 [$\nu_s(COO^-)$], 800 [$\delta(COO^-)$], 740 [$\rho_w(COO^-)$]
I	1552 sh	1365[a]	–	707	3347, 3215, 3107 [ν(N−H)]	3046 [$\nu_{as}(CH_2)$], 2937 [$\nu_s(CH_2)$], 1437 [$\delta(CH_2)$], 1272 [$\rho_w(CH_2)$], 1195 [ν_{as}(C−C)], 990, 932 [ν_s(C−C)], 973 [$\rho(CH_2)$]	1587 [$\nu_{as}(COO^-)$], 1365[a] [$\nu_s(COO^-)$], 814 [$\delta(COO^-)$], 742 [$\rho_w(COO^-)$]
$Ni(A)\cdot 2H_2O$					3462 [ν_{as}(O−H)], 3204 [ν_s(O−H)], 896, 863 [$\rho_r(H_2O)$], 673, 638 [$\tau(H_2O)$], 576 (ρ_wH_2O)	3027 [$\nu_{as}(CH_2)$], 2915 [$\nu_s(CH_2)$], 1453 [$\delta(CH_2)$], 1286 [$\rho_w(CH_2)$], 1178 [ν_{as}(C−C)], 972 [$\rho(CH_2)$] 949 [ν_s(C−C)]	1567 [$\nu_{as}(COO^-)$], 1380 [$\nu_s(COO^-)$], 794 [$\delta(COO^-)$], 731 [$\rho_w(COO^-)$]
II	1565	1382[a]	–	704	3400 [ν_{as}(OH)], 3161 [ν(N−H)], 655 [$\tau(H_2O)$]	1434 [$\delta(CH_2)$], 1281 [$\rho_w(CH_2)$], 1163 [ν_{as}(C−C)], 983 [$\rho(CH_2)$], 957 [ν_s(C−C)]	1586 [$\nu_{as}(COO^-)$], 1382[a] [$\nu_s(COO^-)$], 803 [$\delta(COO^-)$], 743 [$\rho_w(COO^-)$]
$Co(A)\cdot 2H_2O$					3459, 3347 [ν_{as}(OH)], 3189 [ν_s(OH)], 853 [$\rho_r(H_2O)$], 672, 637 [$\tau(H_2O)$], 575 [$\rho_w(H_2O)$]	3027 [$\nu_{as}(CH_2)$], 2945, 2916 [$\nu_s(CH_2)$], 1450 [$\delta(CH_2)$], 1284 [$\rho_w(CH_2)$], 1174 [ν_{as}(C−C)], 972 [$\rho(CH_2)$], 945 [ν_s(C−C)]	1567 [$\nu_{as}(COO^-)$], 1374 [$\nu_s(COO^-)$], 777 [$\delta(COO^-)$], 722 [$\rho_w(COO^-)$]
III	1554	1351	–	698	3293 [ν(N−H)], 2052 [ν(NCS)], 636 [$\tau(H_2O)$], 596 [$\rho_w(H_2O)$]	1443 [$\delta(CH_2)$], 1295 [$\rho_w(CH_2)$], 1163 [ν_{as}(C−C)], 960 [ν_s(C−C)]	1620 [$\nu_{as}(COO^-)$], 1386 [$\nu_s(COO^-)$], 778 [$\delta(COO^-)$]
$Cu(G)\cdot 3H_2O$					3421 [ν(O−H)], 1627 [δ(O−H)], 817 [$\rho_r(H_2O)$], 692 [$\tau(H_2O)$], 520 [$\rho_w(H_2O)$]	2941 [$\nu(CH_2)$], 1458 [$\delta(CH_2)$], 1300, 1280 [$\rho_w(CH_2)$], 1207, 1156 [ν(C−C)], 1014 [$\rho(CH_2)$]	1595 [$\nu_{as}(COO^-)$], 1414 [$\nu_s(COO^-)$], 800 [$\delta(COO^-)$], 765 [$\rho_w(COO^-)$]

Table 2. (Contd.)

Compound	Thioamide bands				Absorption bands of water, ν(NH), and ν(NCS)	Absorption bands of anions	Absorption bands of COO^-
	I	II	III	IV			
IV	–	1348	–	789	3409 [ν(O−H)], 3310, 3261, 3195 [ν(N−H)], 2082 vs [ν(NCS)], 1657 [δ(O−H)], 642 [$\tau(H_2O)$], 522 [$\rho_w(H_2O)$]	1462 [$\delta(CH_2)$], 1292, 1261 [$\rho_w(CH_2)$], 1182 [ν(C−C)]	1714 [ν(C=O)], 1583 [$\nu_{as}(COO^-)$], 1514 [$\nu_s(COO^-)$], 812 [$\delta(COO^-)$], 730 [$\rho_w(COO^-)$]
Ni(G)·3H_2O					3391, 3214 [ν(O−H)], 894 [$\rho_r(H_2O)$], 683, 651 [$\tau(H_2O)$], 559 [$\rho_w(H_2O)$]	2948 [$\nu(CH_2)$], 1467 [$\delta(CH_2)$], 1293 [$\rho_w(CH_2)$], 1199 [ν(C−C)], 1035 [$\rho(CH_2)$]	1567 [$\nu_{as}(COO^-)$], 1405 [$\nu_s(COO^-)$], 834, 818 [$\delta(COO^-)$], 737 [$\rho_w(COO^-)$]
V	1543	1314	–	701	3384, 3278, 3169 [ν(N−H)]	2958 [$\nu(CH_2)$], 1449 sh [$\delta(CH_2)$], 1267 sh [$\rho_w(CH_2)$], 1208 [ν(C−C)], 1048 [$\rho(CH_2)$]	1632 [$\nu_{as}(COO^-)$], 1401 [$\nu_s(COO^-)$]
Co(G)·3H_2O					3343 [ν(O−H)], 870 [$\rho_r(H_2O)$], 689, 651 [$\tau(H_2O)$], 577 [$\rho_w(H_2O)$]	2981 [$\nu(CH_2)$], 1462 [$\delta(CH_2)$], 1294, 1247 [$\rho_w(CH_2)$], 1156 [ν(C−C)], 1030 [$\rho(CH_2)$]	1559 [$\nu_{as}(COO^-)$], 1400 [$\nu_s(COO^-)$], 831, 805 [$\delta(COO^-)$], 736 [$\rho_w(COO^-)$]
VI	1533	1343	1004 sh	699	3421, 3172 [ν(N−H)], 2076 s [ν(NCS)]	2947 [$\nu(CH_2)$], 1248 [$\rho_w(CH_2)$], 1149 [ν(C−C)], 1052 [$\rho(CH_2)$]	1632 [$\nu_{as}(COO^-)$], 1401 [$\nu_s(COO^-)$]

[a] Both thiosemicarbazide and carboxylate anion contribute to the band.

Very strong bands at 2052 (**III**), 2082 (**IV**), and 2076 (**VI**) cm^{-1} were assigned to the formed four-membered rings containing sulfur and nitrogen atoms of deprotonated thiosemicarbazide molecule [8, 9, 12].

The type of carboxylate groups coordination could be elucidated from the value of $\Delta\nu = (\nu_{as} - \nu_s)$ (ν_{as} and ν_s being the carboxylate stretching bands) [17]. However, the $\Delta\Delta\nu$ (COO^-) parameter (difference between the above-mentioned gap in the spectra of the heteroligand complex and the starting carboxylate) seemed more convenient. In the cases of copper complexes, the $\Delta\Delta\nu(COO^-)$ values were negative, whereas they were positive in the cases of nickel and cobalt complexes (Table 2); that suggested bidentate coordination of the carboxylate anions in the nickel(II) and cobalt(III) complexes and the carboxylates ions exclusion to the outer sphere in the cases of copper(II) complexes.

The same was directly confirmed in the case of nickel(II) malonate complex by the X-ray diffraction data [15]. The ν(C=O) absorption band appearing in the spectrum of complex **IV** evidenced about partial protonation of glutarate anion upon formation of the complex between copper(II) glutarate and thiosemicarbazide (proton transfer from thiosemicarbazide to glutarate anion).

IR spectra of the water-containing complexes revealed a number of the related vibration bands, but their interpretation was hardly possible due to complex system of the formed hydrogen bonds and the associated spectral changes.

The bands position in diffuse reflection spectra of the complexes (Table 3) corresponded to pseudo tetrahedral structure of the copper(II) complexes **I** and **IV** and to octahedral of the other compounds [18]. The spectrum of compound **II** contained both the bands corresponding to square and octahedral coordination, in line with X-ray diffraction data.

Thermogravimetric analysis (Table 4) revealed the presence of different kinds of bound water in complex **II**. The lowest-temperature endothermic effect occurred in two stages of mass loss. The first stage of 10.0% (7 water molecules are equivalent to 10.45%

according to calculation); likely, the outer sphere water was eliminated at that stage. The second stage of dehydrating was accompanied by 4.5% mass loss, corresponding to 3 water molecules. Apparently, one of the inner sphere water molecules was eliminated at later thermolysis stage. In the cases of compounds **III** and **IV**, containing water as well, separate stages of dehydration were not observed (Schemes 1, 2).

A specific feature of TGA curves of all the studied complexes was the specimen mass increase during some of the exothermic stages at $T > 450$°C. That could be assigned to formation of metal nitrides or carbides as thermolysis intermediate; their further conversion into oxides would be accompanied by the mass gain.

Thermal stability of the malonate-thiosemicarbazide complexes decreased in the following series: Co > Ni > Cu; in the case of glutarate complexes, the stability series was as follows: Cu > Co > Ni.

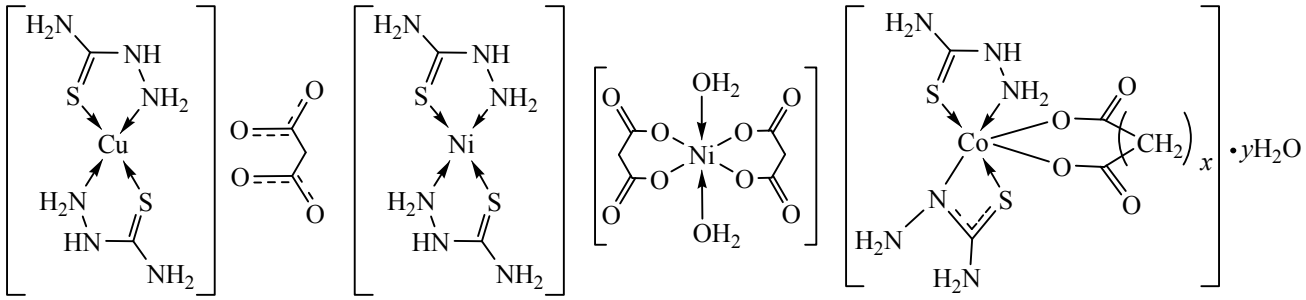
Basing on the above-discussed results, the suggested schemes of the complexes formation and the products structures are as follows.

Table 3. Parameters of diffuse reflection spectra of compounds **I–VI**

Comp. no.	λ, nm	Assignment
I	1189	
	1668	
	2079	
II	502.5	$^3A_{2g} \rightarrow {}^3T_{1g} + \nu_1$
	1114	$^3A_{2g} \rightarrow {}^3T_{2g}$
III	900	$^1A_{1g} \rightarrow {}^3T_1$
IV	1571	
	2069	
V	569	$^3A_{2g} \rightarrow {}^3T_{1g}$
	925	$^3A_{2g} \rightarrow {}^3T_{2g}$
VI	1188	$^1A_{1g} \rightarrow {}^3T_1$

$$Na_2[Cu(A)_2] + 2HL = [Cu(HL)_2](A) + Na_2A, \quad (1)$$
I

Scheme 1.



Scheme 2.

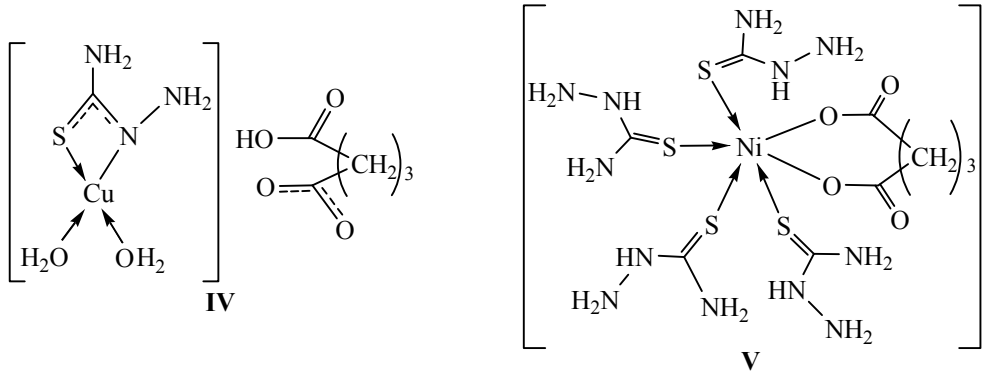


Table 4. Thermally induced transformations of compounds **I–VI**

Comp. no.	Endothermic effects		Exothermic effects		Total mass loss, %
	T range (extreme), °C	Δ*m*, %	*T* range (extreme), °C	Δ*m*, %	
I	85–115(100)	5	110–210(160)	30.5	62.5
	230–350(280)	14	470–580(560)	8.5	
			580–720(670)	+10	
II	120–220(160)	10.0 + 4.5	290–380(330)	5.5	71.3
	220–270(240)	13.6	380–450(420)	10.0	
	270–290(280)	18.6	450–540(455)	+2.5	
	830–920(870)	10.0	540–570(560)	+2.5	
			830–920(870)	10.0	
III	150–200(170)	32.2	510–560(540)	14.9	81.3
	260–350(320)	7.4	560–600(580)	+3.2	
			800–1000	10.4	
IV	140–160(150)	7.4	200–260(220)	21.1	73.8
	290–500(440)	7.4;15.3	500–650(560)	23.1; +10.0	
			860–1000	3.7	
V	70–90(80)	4.0	180–250(200)	12.4	73.8
	110–130(120)	7.4	300–340(320)	6.4	
			500–700(550)	27.7; +1	
			700–1000	4.1	
VI	100–120(110)	3.6	180–270(220)	28.2	76.3
			540–720(620)	25.1	
			720–1000	+0.8; 2.6	

$$4NiA + 4HL + 11H_2O = [Ni(HL)_2]_2[Ni(A)_2(H_2O)_2]_2 \cdot 7H_2O, \quad (2)$$
II

$$4CoX + 8HL + O_2 + nH_2O = 4[Co(HL)L(X)] + (n+2)H_2O, \quad (3)$$
III, VI

$X = A^{2-}$, $n = 1$ (**III**); $X = G^{2-}$, $n = 0$ (**VI**).

$$CuG + HL + 2H_2O = [CuL(H_2O)_2](HG), \quad (4)$$
IV

$$NiG + 4HL = [Ni(HL)_4(G)]. \quad (5)$$
V

EXPERIMENTAL

IR spectra were recorded using the FTIR-8400S spectrometer (Shimadzu), the samples were prepared in the form of pellets with KBr. Diffuse reflection spectra were registered using the Lambda-9 spectrophotometer (Perkin-Elmer) with MgO as reference (β_{MgO} 100%). TGA curves were obtained using the Paulik–Paulik–Erdey derivatograph (in air, at 10 deg/min). The metal content was determined by complexometric titration [19], nitrogen was found by the Dumas method [20], and sulfur was quantified by the Schoeniger method [20].

All the chemicals used were of *analytical pure* grade.

Complexes I–VI. 1.82 g of thiosemicarbazide (0.02 mol) was dissolved in 100 mL of water upon heating. The solution was cooled down to room temperature, and 0.01 mol of crystalline metal malonate or glutarate was added portionwise upon stirring. The mixture was then stirred to equilibrium; the formed precipitate was filtered off, washed with tiny amount of water, and dried over $CaCl_2$ to constant mass.

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