Coordination Compounds of Some 3d-Transition Metal Ions with N^1-[4-(4-bromo-phenylsulfonyl)-benzoyl]-N^4-(4-methoxyphenyl)-thiosemicarbazide

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The paper presents the synthesis and characterization of Cu(II), Co(II), Ni(II), Cd(II), Zn(II) and Hg(II) complexes with N^1-[4-(4-bromo-phenylsulfonyl)-benzoyl]-N^4-(4-methoxyphenyl)-thiosemicarbazide. The new compounds were characterized by IR, EPR, electronic spectroscopy, magnetic moments, thermo-gravimetric analysis and elemental analysis.

Keywords: complexes, acyl-thiosemicarbazide, electronic spectra

Thiosemicarbazide complexes and especially those of 1,4-substituted thiosemicarbazides are of great interest due to their biologic activity, such as anti-bacteria [1], anti-fungi [2], and anti-tumoral [3]. In many cases, the biologic activity of the ligand may be modified by complexation to various metallic ions, as a consequence of blocking the electrons of the donor atoms [4]. This type of ligands may form coordination compounds with metallic ions acting as bidentate ligands by enolization/tioenolization or as monodentate ligands by one oxygen or sulphur atom.

In this paper the synthesis and characterization of Co(II), Cu(II), Ni (II), Cd(II), Zn(II) and Hg(II) complexes with the ligand N^1-[4-(4-bromo-phenylsulfonyl)-benzoyl]-N^4-(4-methoxyphenyl)- thiosemicarbazide, L$_1$, is presented (fig.1).

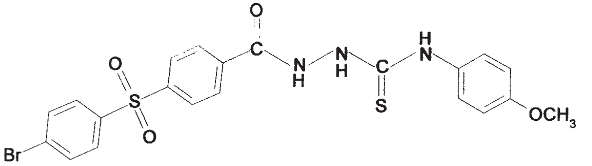

Fig. 1. N^1-[4 -(4-bromo-phenylsulfonyl)-benzoyl]-N^4-(4-methoxyphenyl)-thiosemicarbazide

Experimental part

Electronic spectra were recorded with a spectrometer UV-VIS JASCO 550V in the range of 200-900 nm, using methanol solutions of $2.5 \cdot 10^{-5}$ M concentration. IR spectra were recorded with the Fourier transform spectrometer BIO-RAD FTIR, in KBr pellet, in the range 4000-400 cm^{-1}. Magnetic moments were determined using the Faraday method. RES spectra were recorded with the ART-6-IFIN spectrometer, on powder, at room temperature. The elemental analysis for C, H, N, and S were carried out with the micro-batchmeter Carlo-Elba LA 118 and the quantitative determination of the metallic ion was realized by atomic absorption spectrometry technique (atomic absorption spectrometer AAS 1-N). Melting points were measured using a Boetius apparatus. Thermal analysis has been carried out with a TGA V5.1A DuPont 2000 derivatograph.

L$_1$ was synthesized by following the method described in reference [5].

General synthesis method of coordination compounds

To a solution of 1 mmol (0.52 g) of L$_1$ in 15 mL ethanol/DMF (1:1) were added 15 mL ethanol solution containing

Table 1

ANALYTICAL DATA OF THE NEW PREPARED COMPOUNDS

No.	Compound	M$_{mol}$ (u.a.m.)	Color	η(%)	%N		%C		%H		%S	
					exp	calc	exp	calc	exp	calc	exp	calc
1	$CuC_{42}H_{38}N_6O_{10}S_4Br_2$ **(1a)** **(1b)** **(1c)** **(1d)**	1138	green	70-82%	7.28 7.33 7.21 7.30	7.16	43.23 43.19 43.32 43.15	43.01	3.15 2.95 3.03 2.98	2.90	11.02 11.10 10.95 10.97	10.91
2	$Cu_2C_{46}H_{48}N_6O_{16}S_4Br_2$ **(2)**	1356	dark green	73%	6.23	6.19	40.93	40.70	3.65	3.53	9.52	9.43
3	$CuC_{22}H_{19}N_4O_5S_3Br$ **(3)**	659	green	69%	8.62	8.49	40.24	40.06	2.93	2.88	14.85	14.56
4	$CoC_{23}H_{20}N_3O_6S_2Br$ **(4)**	637	yellow green	80%	6.82	6.59	43.43	43.30	3.33	3.13	10.08	10.04
5	$NiC_{23}H_{20}N_3O_6S_2Br$ **(5)**	637	kaki	78%	6.84	6.59	43.53	43.32	3.28	3.13	10.12	10.04
6	$CdC_{23}H_{20}N_3O_6S_2Br$ **(6)**	690	yellow white	83%	6.45	6.08	40.7	40.0	3.05	2.89	9.42	9.20
7	$ZnC_{42}H_{34}N_6O_8S_4Br_2$ **(7)**	1103	yellow	81%	7.90	7.61	46.25	45.7	3.58	3.08	11.82	11.60
8	$HgC_{42}H_{34}N_6O_8S_4Br_2$ **(8)**	1146	yellow	77%	7.63	7.33	44.54	44.0	3.11	2.96	11.40	11.16

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1 mmol of the salt of the respective ion [$CuCl_2$(a), $CuBr_2$(b), $Cu(NO_3)_2$(c), $CuSO_4$(d), $Cu(CH_3COO)_2$, CuSCN, $Co(CH_3COO)_2$, $Ni(CH_3COO)_2$, $Cd(CH_3COO)_2$, $ZnCl_2$ and $Hg(CH_3COO)_2$] (in the case of [$CuL_1(SCN)(H_2O)$] (**3**), the salt of the metallic ion was dissolved in 5 mL NH_3 25%). The reaction mixture was stirred, at reflux, for 1-2 hrs. The precipitates (of different colors) were filtered, washed with hot ethanol and ethylic ether and dried at 105°C. All complexes have melting points higher than 250°C.

The data of the elemental analysis (table 1) confirm the molar $M:L_1$ combination of 1:1 or 1:2.

Results and Discussions

The thermal analyses for compounds **1-8** are similar. The elimination of ligands takes place in the 240-610 °C range, in two consecutive, sometimes cumulated, steps.

Combinations (**1a-d**) have similar IR spectra. Thus, it is observed the shift of the 1681 cm^{-1} frequency attributed to the $\nu_{C=O}$ vibration, the disappearance of the band from 3186 cm^{-1} attributed to the ν_{N^1H} vibration, due to the deprotonation by complexation, and the occurrence in the spectra of the complex combinations of a relatively intense band at approx. 1618 cm^{-1}, due to the stretching modes of the C=N bond. The occurrence of these frequencies indicates the bidentate mono-negative coordination of the ligand.

For (**2**), (obtained using $Cu(CH_3COO)_2$), two specific bands corresponding to the vibration of C=O and C-O are observed at 1536 cm^{-1}, 1432 cm^{-1} respectively. The difference between these two frequencies, Δ, of 104 cm^{-1}, indicates the bridge coordination of the ion CH_3COO^- [6a].

In the spectrum of (**3**), (prepared from CuSCN), two absorption bands at 695 cm^{-1} and 443 cm^{-1}, specific to the S-coordinated thiocyanate group is noted [6b]. No absorption is noted in the 870-780 cm^{-1} range, so the N-coordination of the thiocyanate is ruled out [6b].

In the spectra of (**4**), (**5**), and (**6**) are found the absorption bands specific to the C=O and C-O from acetate groups at 1524cm^{-1}, 1419cm^{-1} for (**4**), 1548 cm^{-1}, 1436 cm^{-1} for (**5**), and 1530 cm^{-1}, 1427 cm^{-1} for (**6**), respectively [6a].

For (**7**) and (**8**) in the IR spectra it is noticed the disappearance of the vibration frequency ν_{N^2H} and the shift

Table 2

THE MAIN VIBRATION FREQUENCIES OF THE LIGAND AND OF THE NEW PREPARED COMPOUNDS

No	Compound	υ_{N^4H}	υ_{N^2H}	υ_{N^1H}	$\upsilon_{N^1-N^2}$	$\upsilon_{C=O}$	υ_{C-O}	$\upsilon_{C=S}$ $\upsilon_{C=S}$ + $\upsilon_{C=N}$	$\upsilon_{C=N}$	υ_{C-S}	υ_{SO2}	υ_{C-Br}
L	$C_{21}H_{17}N_3O_4S_2Br$	3452	3315	3186	1011	1681	_	754 1251	_	_	1158	574 616
1	**(1a)** **(1b)** **(1c)** **(1d)**	3452 3451 3452 3460	3272 3270 3266 3265	_	1010 1010 1011 1010	_	1430 1431 1430 1432	758, 1246 756, 1245 754, 1243 756, 1245	1618 1607 1617 1606	_	1158 1156 1159 1158	567, 617 566, 617 557, 618 573, 614
2	**(2)**	3444	3267	_	1011	1536	1432	758 1246	1605	_	1162	557 616
3	**(3)**	3461	3265	_	1011	_	1428	756 1246	1606	_	1162	556 617
4	**(4)**	3557	3283	_	1010	1530	1427	754 1244	1570	_	1158	576 615
5	**(5)**	3425	3280	_	1009	1524	1419	752 1243	1597	_	1156	575 615
6	**(6)**	3475	3266	_	1010	1548	1436	756 1247	1605	_	1159	576 614
7	**(7)**	3478	_	3310	1009	1642	_	_	1620	674	1150	576 615
8	**(8)**	3453	_	3312	1010	1630	_	_	1617	628	1154	565 617

Table 3

THE ASSIGNMENT OF THE ELECTRONIC TRANSITIONS IN COMPOUNDS **(1) – (8)**

No.	Complex	Transitions d-d (cm^{-1})			Geometry
1		$d_{x^2-y^2} \to d_{z^2}$,	$d_{x^2-y^2} \to d_{xy}$,	$d_{x^2-y^2} \to d_{xz}, d_{yz}$	octahedral
	(1a) **(1b)** **(1c)** **(1d)**	11312 11308 11310 11314	14720 14705 14715 14723	_ _ _ _	
2	**(2)**	11235	13120	15600	axially distorted octahedral
3	**(3)**	$d_{xy} \to d_{xz}, d_{yz}$	$d_{xy} \to d_{z^2}, d_{x^2}-y^2$	-	distorted tetrahedral
		13510	14290		
4	**(4)**	$^4A_2 \to {}^4T_1(F)$	$^4A_2 \to {}^4T_1(P)$	$^4A_2 \to {}^4T_2(F)$	distorted tetrahedral
		11280	16310	-	
5	**(5)**	$d_{x^2-y^2} \to d_{z^2}$,	$d_{x^2-y^2} \to d_{xy}$,	$d_{x^2-y^2} \to d_{xz}, d_{yz}$	square planar
		-	14620	23370	
6	**(6)**	n - π^*		π - π^*	distorted tetrahedral
		27250		36760	
7	**(7)**	27030		36750	distorted tetrahedral
8	**(8)**	27200		37170	distorted tetrahedral

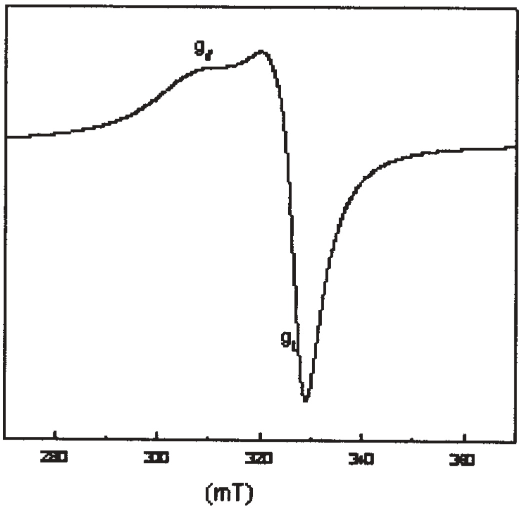


Fig. 2. The RES spectrum of **(3)** on crystalline powder, at room temperature

towards lower wave numbers of the vibration frequency specific to the group C=O (1642 cm^{-1}, 1630 cm^{-1}, respectively), as well as the shift of the vibration frequency $\nu_{C=S}$ and of the associated band $\nu_{C=S} + \nu_{C=N}$. Besides, in the IR spectra of these two combinations occur bands specific to the vibration frequency $\nu_{C=N}$, at 1620 cm^{-1}, 1617 cm^{-1}, respectively, and to the vibration frequency $\nu_{C-S,}$ at 674 cm^{-1}, 628 cm^{-1}, respectively. The occurrence of these frequencies indicates the mononegative bidentate coordination of the ligand. In table 2 the main vibration frequencies of the ligand and of the new compounds, together with their assignments, are presented.

The absorption bands specific to the d-d transitions, according to literature data [7], are presented in table 3. These data suggest that **1a, 1b, 1c,** and **1d** are octahedral, a fact proven also by the values of the tensor {g}. The complex (**2**) has an axially deformed octahedral geometry (D_{4h}) proven by the occurrence of the absorption bands at 11235 cm^{-1}, 13120 cm^{-1}, 15600 cm^{-1}, respectively, assigned to the $d_{x^2-y^2} \rightarrow d_{z^2}$, $d_{x^2-y^2} \rightarrow d_{xy}$ and $d_{x^2-y^2} \rightarrow d_{xz}, d_{yz}$ transitions.

Table 4

THE VALUES OF THE {g}PARAMETERS FOR COMPOUNDS **(1)** - **(3)**

Complex	g_i	$g_{\parallel}$	$g_{\perp}$	μ_{ef}(MB)	G
(1a)	2.09	-	-	2.59	-
(1b)	2.08	-	-	2.57	-
(1c)	2.09	-	-	2.45	-
(1d)	2.07	-	-	2.37	-
(2)	-	2.30	2.09	1.45	3.33
(3)	-	2.27	2.06	2.43	4.50

The absorption bands in the electronic spectrum of (**3**), at 13510 cm^{-1} and 14290 cm^{-1} confirm the tetrahedral geometry of the Cu(II) ion.

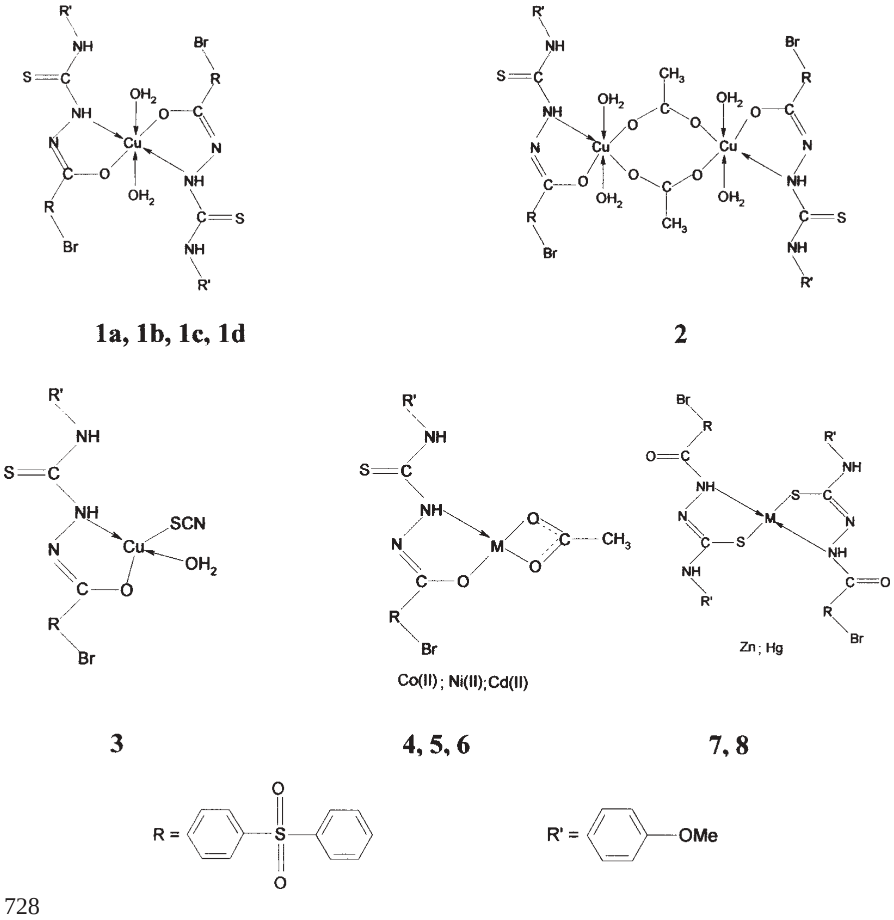
The electronic spectrum of compound (**4**) exhibits two bands assigned to the transitions $^4A_2 \rightarrow {}^4T_1$ (F) and $^4A_2 \rightarrow {}^4T_1$(P), confirming the pseudo-tetrahedral geometry of the Co(II) [7]. The nickel compound (**5**) has a plane-square geometry proven by the presence of the absorption bands from 14620 cm^{-1} and 23370 cm^{-1} [8].

The UV-VIS spectra of (**6**), (**7**) and (**8**) exhibit absorption bands specific to some inter-ligand electronic transitions of the n - π^* and π - π^* type with a bathochrome shift relative to the free ligand.

The RES spectra in X-band of the copper complexes were recorded on crystalline powder, at room temperature. The values of the {g} tensor (determined using the method presented in [9, 10]) and of the magnetic moments are presented in Table 4.

Figure 2 shows the RES spectrum of (**3**).

The shape of RPE spectra for **1a, 1b, 1c,** and **1d** are very similar, leading to close values of the {g} tensor, which are specific to an octahedral geometry of the Cu(II) ion. The values of the magnetic moments for these combinations are in the range of 2.37-2.59 MB, characteristic for an un-coupled electron of a copper ion, but also for an orbital contribution to the value of the



1a, 1b, 1c, 1d

2

3

4, 5, 6

7, 8

Fig. 3. Structural formulae of the compounds reported in this paper

magnetic moment. The values of the tensor $g\parallel$ and $g\perp$ were determined from the shape of the RPE spectrum of (**2**) (table 4). The parameter $G = (g\parallel -2) / (g\perp -2) = 3.33$, indicates an exchange interaction between the copper centers. In a D_{4h} geometry, this $G < 4$ value can be explained taking into account the existence of some exchange interactions between the two copper centers or super-exchange interactions between the two copper centers through the acetate bridge [11,12]. This statement is in agreement with the value of the magnetic moment (1.45 MB) which indicates an anti-ferromagnetic interaction between the two copper centers. It is known the fact that the term of the fundamental state, occupied by paramagnetic e^-, determined the values of the $g\parallel$ and $g\perp$ parameters. If paramagnetic e^- of the Cu(II) ion is in the ground state $B_{1g}(d_{x^2-y^2})$, then $g\parallel > g\perp > 2.002$ [13-15]. For (**2**) it is noticed that $g\parallel > g\perp > 2.002$, which means that the term of the ground state is of $B_{1g}(d_{x^2-y^2})$, in an axially distorted octahedral geometry. The value of the G parameter is higher than 4 ($G = 4.50$) in the case of the complex combination (**3**) which means that the exchange interactions are negligible.

Correlating the data obtained in the physico-chemical determinations, the following structural formulae are proposed for the coordination compounds reported in figure 3.

Conclusions

The paper presents the synthesis and characterization of coordination compounds of Cu(II), Co(II), Ni(II), Cd(II), Zn(II), and Hg(II) with N^1-[4-(4-bromo-phenylsulfonyl)-benzoyl]-N^4-(4-methoxyphenyl)- thiosemicarbazide.

The compounds (**1a**), (**1b**), (**1c**), and (**1d**) have an octahedral geometry, proven by IR and UV-VIS spectroscopies, as well as by the similar values of the tensor $\{g_i\}$. In these complexes, the ligand coordinates mononegative bidentate at the metallic ion by the N^2 atom and the oxygen atom.

The compound (**2**) has an axially distorted octahedral geometry, proven by electronic spectra, as well as by the values of the $g\parallel$ and $g\perp$ parameters. In this complex, the ligand coordinates bidentately mononegative as well.

Spectral data indicate, for (**3**), (**4**), (**5**), and (**6**) a tetrahedral coordination around the metallic ion and a molar ratio of $M:L_1 = 1:1$.

In the case of (**7**) and (**8**), the ligand also coordinates bidentately mononegative, through N^1 and the sulphur atom.

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