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SCIENTIFIC WORK

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METAL COMPLEXES OF 3-CHLORO-4--HYDRAZINO-CARBONYL-METHOXY--BENZENESULFONDIBUTHYLAMIDE

By taking the biological activity of 3-chloro-4-hydrazinocarbonyl-methoxy-benzenesulphondibuthylamide and of some transitional metals (Cu, Co, Cr, Fe, Mn, Ni, Sn) into account we considered it useful to capitalize the already obtained hydrazide by complexion reactions with various metallic salts. The reaction was carried out in the organic solvent medium, by heating under stirring. The obtained products were purified by recrystallization from organic solvents (especially ethanol) and characterized by means of melting points, elemental analysis and spectral measurements.

Key words: 3-chloro-4-hydrazinocarbonyl-methoxy-benzenesulphondibuthylamide, transitional metal complexes, transitional metals salts (Cu, Co, Cr, Fe, Mn, Ni, Sn).

The researches on obtaining new biologically active compounds with potential applications of herbicides, growing biostimulants, fungicides, and acaricides have been much developed recently. Among various chemical compounds studied lately the aryloxyalkylcarboxylic acids and their derivatives are particularly important, their herbicidal and auxinic actions being well known for a long time.

By introducing sulphonamidic groups into the molecules of phenoxyacetic, chlorophenoxy acetic, cresoxyacetic, xylenoxyacetic, α-phenoxypropionic and γ--phenoxybutiric acids, the auxinic and selective herbicidal properties of phenoxyalkan carboxylic derivatives have been improved along with the lack of toxic residues and the toxicity towards humans and animals [1,4].

Important progresses were made by using some hydrazides of phenoxyacetic acids, which were for the first time synthesized by Baltazzi and Delavigne [2] in 1955. By condensing the hydrazides with some transitional metals (Cu, Fe, Cr, Co, Mn) a series of metallic complexes were obtained which were proved to be efficient on treating various diseases [5,6].

Drugs containing Cu complexes are used in inflammatory processes such as rheumatic arthritis, osteoarthritis, and rheumatologic fever. They are also used for ulcerous, convulsions, and cancer and diabet treatments. It is believed that the positive effects are due to the Cu complexes that promote tissue reparation processes, which requires Cu dependent enzymes. Copper also makes it possible for our body to absorb the iron necessary for hemoglobine synthesis. Cu is also necessary for forming elastine and proteins as components of various tissues and contributes to the development of bones [7,8].

The iron is a constituent of blood pigment - hemoglobine, other ferments and various enzymes. Fe is also a catalyst that assists all kinds of chemical transformations in the human body. It also contributes to maintaining several immunity system functions [7,8]. The cobalt is a bioactive element that is a part of B_{12} vitamin, being necessary for blood forming processes [7,8]. The chromium (Cr) is needed in human body as a stimulator acting on nucleic acid transformations; it is also a part of human skin, muscles, lipids and of fermentative systems [7,8]. The manganese (Mn) is a part of some ferments in the human body and activates destructive processes of protein materials. It also participates in bone, tissue and cartilage forming, in glycemic regulation and has a neurostimulative action [7,8].

By taking into account the practical importance of metallic complexes and their easiness to release metal in the living organism we have continued with the researches by obtaining some metal complexes of aminosulphonyl-phenoxyacetic acids hydrazones [5,6]. The transitional metal containing product shows a dual action due to the starting hydrazone, on one hand, and the metal presence, on the other. The compounds have not been tested for their biological acti-

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vity yet. The hydrazone activity is to be estimated in the near future in co-operation with the University of Agriculture "Ion Ionescu de la Brad" of Iasi, while that of the obtained complexes and of the starting metals will be assessed in co-operation with the University of Medicine and Pharmacy "G. T. Popa" of Iasi.

EXPERIMENTAL

General procedure

0.783 g (0.002 mol) of 3-chloro-4-hydrazinocarbonyl-methoxy-benzenesulphondibuthyl-amide was solved in 15 ml of acetone and 0.0013 mol inorganic salt was solved in 5 ml of water. The reaction mixture was heated for about 15 min in the water bath under stirring. The solution was left at room temperature over night. The precipitate was filtered and washed on the filter with water (in order to eliminate the inorganic salt left over) and with ethyl ether. The obtained product was purified by recrystallisation from ethanol or acetone [9,10].

Tin(II) 3-chloro-4-hydrazinocarbonylmethoxy-benzenesulfondibuthylamidate

0.783 g hydrazide, solved in acetone, and 0.247 g (0.0013 mol) tin chloride solved in 5 ml of water were heated under stirring, as described above. The precipitate separated was filtered, washed with water and ethanol and recrystalised from acetone. White crystals, melting at 104 °C, were obtained.

Copper(II) 3-chloro-4-hydrazinocarbonylmethoxy-benzenesulfondibuthylamidate

0.783 g hydrazide was mixed with 0.236 g (0.0013 mol) copper acetate solved in 5 ml of water and the reaction proceeded such as described in the general procedure. The next morning a precipitate separated was filtered, washed on the filter and purified from ethanol. Finally, a green powder was obtained, m.p= 110°C.

Cobalt(II) 3-chloro-4-hydrazinocarbonylmethoxy-benzenesulfondibuthylamidate

0.783 g hydrazide, solved in 15 ml of acetone, reacted with 0.230 g (0.0013 mol) cobalt acetate solved in 5 ml of water as presented above. The pink final product was filtered and washed with water. The raw product was recrystallised from acetone. A pink powder was finally obtained; m.p = 99-100 °C.

Nickel(II) 3-chloro-4-hydazinocarbonylmethoxy-benzenesulfondibuthylamidate

0.783 g hydrazide, solved in acetone, and 0.169 g (0.0013 mol) nickel chloride solved in 5 ml of water were heated under stirring, as described above. The precipitate separated was filtered, washed with water and ethanol, and recrystalised from acetone. White crystals were obtained; m.p. = 268 °C.

Iron(III) 3-chloro-4-hydrazinocarbonylmethoxy-benzenesulfondibuthylamidate

0.783 g hydrazide, solved in acetone, was mixed with a solution obtained from 0.211 g (0.0013 mol) iron chloride and of 5 ml water. The reaction occurred as described in the general procedure. The separated solid was filtered, washed with water and purified by recrystallisation from acetone. Yellow crystals were obtained; m.p. = 153-156 °C.

Chromium(II) 3-chloro-4-hydrazinocarbonylmethoxy-benzenesulfondibuthylamidate

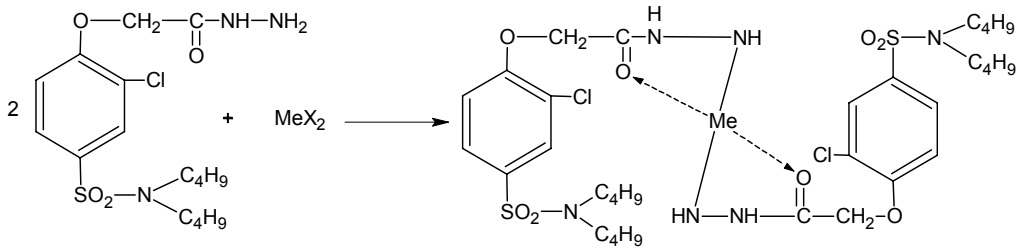
0.783 g hydrazide, solved in acetone, and 0.321 g (0.0013 mol) chromium acetate solved in 5 ml of water were heated under stirring, as described above. The precipitate separated was filtered, washed with water and ethanol on the filter and finally recrystallised from acetone. White crystals were obtained; m.p. = 104-106 °C.

Manganese(II) 3-chloro-4-hydrazinocarbonylmethoxy--benzenesulfondibuthylamidate

0.783 g hydrazide reacted with 0.163 g (0.0013 mol) manganese chloride solved in 5 ml of water, as described above. The precipitate, separated in time, was filtered, washed on filter with water, dried and recrystalised from ethanol. A white powder was obtained; m.p. = 105-108 °C.

RESULTS AND DISCUSSION

Starting from hydrazides of sulphonamidated phenoxyacetic acids previously synthesized [4,9,11], and considering their biological activity, we set our goal to obtain metal complexes according to the following reaction scheme:



where: Me = Cu, Co, Cr, Fe, Mn, Ni or Sn and X = Cl or CH_3COO.

Some physicochemical properties of the obtained metal complexes and the results of the elemental analysis are presented in Table 1. The products were finally purified by recrystallisation from organic solvents and then submitted to UV, IR and NMR spectral measurements. The compound structure was verified by means of FT-IR spectra. The IR spectra show all the characteristic bands for the synthesized compounds. (Table 2). Thus, the stretching vibration bands for C=C were to be found in the 1583.55--1637.56 cm^{-1} range, as a strong or a very strong band. Vibration bands of C=O and C=N bonds were found between 1654.92-1672.28 cm^{-1}, as very strong bands. The C=S bands were shown between 1099.42 and 1105.21 cm^{-1}. The peaks corresponding to $-SO_2-NH-$ group appeared at 1155.36-1159.22 cm^{-1}, and those for Ar-O were found at 1220.94-1253.73 cm^{-1}. The S=O and S-N bonds showed between 1060.85 and 1101.35 cm^{-1}. The deformation ring vibration bands showed at 418.55-601.79 cm^{-1} and between 914 and 1002.35 cm^{-1}. Vibration bands for νNO_2 sym. were to be found in the 1317.38 and 1342.45 cm^{-1} range, as very strong bands. The valence vibration bands for C-N appeared at 1105.21-1138.00 cm^{-1} and for C-OH bonds at 1018.41 cm^{-1}. The deformation vibration bands for δCH_3 sym. and δCH_3 asym. have medium and strong absorptions around 1375.24 cm^{-1} and 1431.18 cm^{-1}, respectively.

Table 1. Physicochemical characteristics of metal complexes and the results of their elemental analysis

MeX_2	Formula	M / g m^{-1}	m.p., °C	Color	Elemental analysis, %					
					C		H		N	
					Calc	Found	Calc	Found	Calc	Found
1. $SnCl_2$	$C_{32}H_{50}N_6O_8S_2Cl_2Sn$	900	104	Yellow	42.68	42.56	5.60	5.71	9.33	9.47
2. $(CH_3COO)_2Cu$	$C_{34}H_{50}N_6O_8S_2Cl_2Cu$	845	110	Dark-green	46.97	46.86	5.80	5.92	9.67	9.79
3. $(CH_3COO)_2Co$	$C_{34}H_{50}N_6O_8S_2Cl_2Co$	839.93	99-100	brown	47.22	47.08	5.83	5,92	9.72	9.86
4. $NiCl_2$	$C_{34}H_{50}N_6O_8S_2Cl_2Ni$	839.71	268	White-green	47.24	47.10	5.83	5.94	9.72	9.85
5. $FeCl_3 \cdot 6H_2O$	$C_{34}H_{50}N_6O_8S_2Cl_2Fe$	837	153-156	Green-yellow	47.39	47.23	5.85	5.97	9.75	9.88
6. $(CH_3COO)_2Cr \cdot H_2O$	$C_{34}H_{50}N_6O_8S_2Cl_2Cr$	833	104-106	Dark-beige	47.60	47.48	5.87	5.99	9.80	9.93
7. $MnCl_2$	$C_{34}H_{50}N_6O_8S_2Cl_2Mn$	836	105-108	Light-beige	47.44	47.28	5.85	5.97	9.75	9.88

Table 2. IR characteristic absorptions for metal complexes

Compound	Characteristic bands (cm^{-1}) and their intensity[a]
1.	443.63 W, 457.13 W, 484.13 M, 520.78 M,530.42 M, 542.00 M, 574.79 S, 601.79 S, 721.38 S, 902.68 W, 918.11 M, 937.40 W, 977.91 W, 1001.05 M, 1026.13 M, 1045.42 M, 1068.56 S, 1103.28 S, 1157.29 VS, 1220.94 M, 1249.87 S, 1261.44 M, 1274.94 M, 1298.09 M, 1342.45 S,1375.24,1429.25, 1587.41 S, 1670.35 VS, 3057.17 W, 3437.14 M
2.	439.77 W, 449.41 W, 480.27 M, 520.78 M, 532.35 M, 553.57 S, 574.79 S, 599.86 S, 725.23 S, 918.11 S, 937.40 M, 987.55 S, 1026.13 S, 1045.42 M, 1074.35 S, 1101.35 S, 1155.36 S, 1253.73 S, 1269.16 S, 1300.02 S, 1342.45 S, 1381.03, 1583.55 VS, 1633.70 VS, 3045.59 VW, 3450.64 M
3.	418.55 VW, 443.63 W, 457.13 W, 486.06 W, 530.42 M, 543.92 M, 574.79 S, 584.43 S, 601.79 S, 723 S, 902.68 W, 920.04 M, 937.40 W, 981.77 W, 1001.05 M, 1026.13 M, 1045.42 M, 1068.56 S, 1103.28 S, 1157.29 VS, 1222.87 M, 1249.87 S, 1274.94 S, 1296.16 M, 1342.45 S,1375.24,1425.39, 1587.41 S, 1670.35 VS, 3057.17 W, 3437.14 M
4.	418.55 W, 441.70 M, 472.56 M, 484.13 M, 524.64 S, 532.35 S, 545.85 S, 578.64 VS, 599.86 VS, 721.38 S, 921.97 S, 977.91 W, 993.34 W, 1028.06 M, 1053.13 M, 1078.21 S, 1101.35 S, 1157.29 VS, 1251.80 S, 1278.80 S, 1300.02 M, 1340.52 S,1388.74,1436.96, 1585.48 M, 1662.64 S, 3689.82 VW
5.	443.63 M, 482.20 M, 522.71 M, 534.28 M, 553.57 S, 578.64 VS, 599.86 S, 725.23 S, 1026.13 S, 1045.42 M, 1070.49 S, 1089.78 S, 1103.28 S, 1159.22 VS, 1238.30 S, 1278.80 S, 1307.73 M, 1342.45 S,1373.31,1431.18 1587.41 S, 1654.92 VS, 3055.24 W, 3406.28 M
6.	441.70 W, 482.20 M, 547.78 S, 574.79 S, 601.79 S, 721.38 S, 979.84 M, 1028.06 S, 1047.34 M, 1068.56 S, 1101.35 S, 1157.29 S, 1247.94 S,1373.31,1433.11, 1608.63 S, 1670.35 S, 3057.17 M, 3446.79 M.
7.	443.63 M, 484.13 M, 503.42 M, 530.42 S, 542.00 M, 572.86 VS, 584.43 VS, 601.79 S, 721.38 S, 902.68 M, 918.11 S, 937.40 M, 977.91 M, 1001.05 S, 1028.06 S, 1035.77 S, 1045.42 S, 1068.56 S, 1103.28 VS, 1157.29 VS, 1220.94 S, 1296.16 S, 1342.45 VS, 1375.24 S, 1587.41 S, 1672.28 VS, 3057.17 M, 3446.79 VW

[a]VS = Very strong; S = strong; M = medium; W = weak; and VW = very weak

CONCLUSION

By taking the biological activity of 3-chloro-4--hydrazinocarbonyl-methoxy-benzenesulphondibuthyl-amide and of some transitional metals (Cu, Co, Cr, Fe, Mn, Ni, Sn) into account, we considered it useful to capitalize the already obtained hydrazide by complexing it with various metallic salts. The reaction was carried out in the organic solvent medium by heating, under stirring. The obtained products were purified by recrystallisation in organic solvents (especially ethanol). The final products are to be further characterized by spectral measurements.

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