CONDENSED HETEROAROMATIC SYSTEMS THAT CONTAIN A THIOPHENE RING COMMUNICATION 29.* NEW COMPLEXING AND CHELATE COMPOUNDS OF BENZO[b]THIOPHENE SERIES

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V. P. Litvinov, Ya. L. Gol'dfarb, and É. G. Ostapenko

Previously [2, 3] we had described some bifunctional derivatives of benzo[b]thiophene, which belong to the series of so-called mercaptoaldimines and can be used to synthesize chelate compounds. This was achieved by inserting the appropriate substituents in the 2 and 3 positions of the thiophene fragment of the molecule, which made it possible to obtain metal chelates with sulfur and nitrogen atoms as the outer coordinating centers.

As an expansion of this research we studied the complexing ability of 3-hydroxy-2-benzo[b]thiophenecarboxaldehyde (I) and its Schiff bases, in this way approximating the systems studied by us to salicylaldehyde, which is widely used to obtain and study the chemical and physical properties of chelate compounds [4]. The problem reduced to replacing the sulfur atom outside the ring in the mercaptoaldimines of the benzo[b]thiophene series by oxygen and tracing the effect of this replacement on the properties of the chelate compounds.

3-Hydroxy-2-benzo[b]thiophenecarboxaldehyde (I), which was obtained from thiosalicylic acid [5] or by the hydrolysis of 3-hydroxy-2-iminomethylbenzo[b]thiophene (II, R = H) [6], when reacted with amines forms the corresponding Schiff bases (II) and (III). The latter, the same as hydroxyaldehyde (I), was used by us [7] to obtain chelates (IV) and (V), respectively. Some of the complexes of the (VI) type were obtained by the reaction of the (V) chelates with amines. This process can be depicted as initial attack of the carbonyl carbon by the amine and subsequent dehydration of the intermediate compound (VII) [8].



*See [1] for Communication 28.

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Chelate	bləiY	رمی (م م) ک	Empirical formula	υ	н		s S		I .	I I		м 	methód*	ance of chelate	Solvent
(V) M=Cu.	92	330-332	C ₁₈ H ₁₀ O ₄ S ₈ Cu	51,81	, 33		5,22 15	63 51	,73 2,	- IV	- 15,	34 15,20	w (acetone)	Dark green crystals	Ethanol, DMF,
(V) M=Co	63	310	C18H10O4S2Co	52,05 2	.64		5,69 14,	10 52	,30 2,	- 44	- 15,	21 14,26	w (methanol)	Brown powder	DMF, DMSO
(V) M=Ni	72	340	C ₁₈ H ₁₀ O ₄ S ₂ Ni	52,20	60		5, 10 13,	71 52.	,33 2,	- 14	- 15,	52 14,21	r (DMF)	Light green powder	Ethanol, DMF,
(v) M = Zn (v) M = Vo	206	260 290	C16H10O4S2Zn C18H10O6S2V	51,12 51,94	36		5,35 15,02 11,	53 51 53	31 2,		12, 12, 12, 12, 12, 12, 12, 12, 12, 12,	28 15,57 22 12,09	w (acetone) tp (DMF)	Yellow powder Light brown powder	DMF, DMSO DMF, DMSO
(VI) M=Cu, R=H	86	217-218	C18H12O2N2S2Cu	51,91	2,746	1 22	5,03 14,	57 51	97 2,	91 6,	73 15,	42 15,27	r (DMF)	Brown crystals	Methanol, DMF
(VI) M=Ni, R=H	80	290	C ₁₈ H12O2N2S2Ni	50,39	3,64		4,78 13,	50 50	38 3,	29 -	- 14,	94 13,68	r (DMF)	Dark green crystals	Acetone, DMF,
(VI) M=Zn, R=H	82	256-258	C ₁₈ H ₁₂ O ₂ N ₂ S ₂ Zn	51,74	2,97 6	177 1	5,41 15	71 51,	74 2,	90 <mark>6,</mark>	65 15,	35 15,65	w (methanol)	Light green crystals	Ethanol, benzene,
(VI) $M=Ni$, $R=C_4H_9$	55	169—170	C26H28O2N2S2Ni	59,81	6,51	1	<u><u></u> <u></u></u>	21 59,	67 5,	- 68	 	- 11,21	r (acetone)	Greenish-yellow	DMF, DMSO
(VI) M=Cu, R=C6H6	57	580	C30H20O2N2S2Cu	63,29	3,784	,86 1	0,71 11	58 63,	42 3,	55 4,	93 11,	29 11,18	r (CHCl ₃)	Dark green crystals	Ethanol, DMF
(VI) M=Zn, R=C ₆ H ₅	20	286	C30H20O2N2S2Zn	64,01	3,70	- 1	1,23 10	98 63,	21 3,		- - -	25 11,47	w (methanol)	Yellow crystals	DMF
$(IV)M=Cu, R'=(CH_2)_2$	60	285-287	C20H14O2N2S2Cu	52,27	3,67		3,92 13	58 52,	22 3,	1	- 13,	94 13,81	r (DMF)	Green crystals	Acetone, DMF,
(IV) M=Ni, R'=(CH ₂) ₂	85	322-324	C20H14O2N2S2Ni	54,46	3,10		4,43 13.	46 54,	95 3,	ा ह्य	- 14,	67 13,43	r (DMF)	Dark greeen crystals	Acetone, DMF,
$(IV) M=Zn, R'=(CH_a)_2$ (IV), M=VO,	8 8 88	400 360	C20H14O2N2S2Zn C20H14O3N2S2ZV	51,90 53,81	,48	<u> </u>	2,64 4,05 11	20 20 20 20	93 3, 93 3,	17	$\frac{11}{14}$	28 40 11,44	r (DMF) r (DMF)	Yellow powder Green crystals	DMF
$ \begin{array}{c} \mathbf{K} = (\mathbf{CH}_2)_2 \\ (\mathbf{IV}) \mathbf{M} = \mathbf{Cu}, \end{array} $	R	330	C22H18O2N2S2Cu-	58,43	44		1,28 11,	01 59,	05 4,	52	- 11,	68 11,57	rp (DMSO)	Dark blue crystals	Pyridine, DMSO
$(1V) M = Z_{\Omega}, R = (CH_2)_4$	36	213-214	C6H5N 7 C22H18O2N2S2Zn	56,08	3,97		- 14	,31 55,	99 3,	84 -	1	- 13,85	rp (DMSO)	Yellow crystals	DMF, DMSO
(IV) $M=Cu$, $R'=-$	97	350	C ₁₈ H ₁₀ O ₂ N ₂ S ₂ Cu	52,00 2	11, 11		5,21 15.	03 52,	44 2,		- 15,	49 15,35	w (acetone)	Brown powder	Pyridine, DMF
(1V) $M=Ni$, $R'=-$	98	400	C ₁₈ H ₁₀ O ₂ N ₂ S ₂ Ni	53,14	,89		, 	- 53	84 2,	100	 	 	w (acetone)	Brown powder	Pyridine, DMF
(IV) $M=Zn$, $R'=-$	86	400	ClsH10O2N2S2Zn	52,10 2	2,75	1	12	,84 51,	99 2,	1	· 	- 15,72	w (acetone)	Yellow crystals	Pyridine, DMF
(1V) M=Cu,	94	380	C24H14O2N2S2Cu	58,77	3,00		3,29 12.	98 58,	82 2,8	1 88	- 13,	09 12,97	r (DMF)	Light brown powder	DMF, DMSO,
$K = 0 - CeH_4$ (IV) $M = Ni, R' = 0$ -	63	380	C24H14O2N2S2Ni	59,75	3,08		3,27 12	,01 59,	41 2,	91	- 13,	22 12,01	r (DMF)	Brown crystals	DMAAM
(IV) M=Zn, $R' = o$	65	420	C24N14O2N2S2Zn	58,77	3,12		2,95 13	,32 58,	60 2,8	37	- 13,	04 13,29	r (DMF)	Orange crystals	DMF, DMAAM
$\begin{array}{c} \operatorname{UoH4}_{0} \\ (\mathrm{IV}) \mathbf{M} = \mathrm{VO}, \mathbf{R}' = o \\ \operatorname{CoH4}_{0} \end{array}$	68	400	C24H14O8N2S2V	58,74	3,14		2,49 -	<u>8</u> 1	42 2,8	۱ 	- 13,	1	r (DMF)	Brown crystals	DMF, DMAAM
 w = washing; rp = rep; t Based on the analysis t Based on the analysis t Based on the analysis ** Dimethylacetamide. 	data data 2%. data	i the com	= recrystallization. pound contains a mole ound contains a mole	scule of cule of	wate	ine.	, , , , ,	- ·		-	-	-	-	-	

TABLE 1

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The chelates (Table 1) obtained by the indicated methods separate as colored powdery or crystalline precipitates that are difficultly soluble in many organic solvents. When heated they decompose in a quite wide temperature range, and only for the zinc compounds can a more or less distinct melting point (decomposition) be indicated.

The problem of the structure of the characterized complexes was not solved conclusively, since it is impossible to exclude the effect of tautomerism of the ligands. In particular, it was shown by us [9] that if the hydroxyaldimines (II) exist in solutions predominantly in the oxo form (VIII), then the aldehyde (I) corresponding to them exists mainly in the hydroxyaldehyde form (I).



EXPERIMENTAL METHOD

3-Hydroxy-2-benzo[b]thiophenecarboxaldehyde (I). Hydroxyaldehyde (I) was obtained as described in [5]: mp 106-107° (from alcohol), and also as described in [6].

<u>N,N'-Bis-(3-hydroxy-2-benzo[b]thenylidene)ethylenediamine (III, R' = $(CH_2)_2$.* To a solution of 3 g of hydroxyaldehyde (I) in 20 ml of alcohol was added 0.49 g of ethylenediamine. The mixture was refluxed for 2 h, and the precipitate was filtered, washed with alcohol, and dried. We obtained 2.1 g (67%) of yellow (III), mp 216° (from DMF). Found: C 63.24; H 4.27; N 7.38; S 16.68%. $C_{20}H_{16}O_2N_2S_2$. Calculated: C 63.13; H 4.24; N 7.36; S 16.85%.</u>

3-Hydroxy-2-(o-hydroxyphenyliminomethyl)benzo[b]thiophene (II, $R = o-C_6H_4OH$). A mixture of 3.57 g of (I), 2.18 g of o-aminophenol, and 120 ml of m-xylene was refluxed in an apparatus equipped with a Dean-Stark trap until all of the water was removed. The residual m-xylene was vacuum-distilled, and

*Here and subsequently the (II) and (III) type of compounds are regarded as belonging to the hydroxyaldimine series, although, as was mentioned above, in solutions they exist predominantly in the oxo form.

the crystalline precipitate was washed with acetone, then with ether, and treated with boiling methanol. We obtained 4.8 g (89%) of (II); after recrystallization from 80-85% DMF and drying in vacuo at 135°, mp 228°. Found: C 66.51; H 4.14; S 11.86%. $C_{15}H_{11}O_2NS$. Calculated: C 66.89; H 4.12; S 11.90%.

<u>N,N'-Bis-(3-hydroxy-2-benzo[b]thenylidene)-o-phenylenediamine (III, R' = $o-C_6H_4$)</u>. To a solution of 12 g of (I) in 15 ml of DMF was added a solution of 3.36 g of o-phenylenediamine in 10 ml of DMF, and then additional DMF was added to a total volume of 50 ml. The mixture was heated at 100° for 1 h, cooled, and the precipitate was filtered, washed in succession with DMF, acetone, and ether, and dried in vacuo over CaCl₂. We obtained 10.5 g (82%) of (III); after recrystallization with DMF, washing with acetone, and drying in vacuo at 135° over P₂O₅, mp 230°. Found: C 66.98; H 3.79; S 14.74%. C₂₄H₁₆O₂N₂S₂. Calculated: C 67.27; H 3.76; S 14.97%.

The following Schiff bases (III) were obtained in a similar manner: N, N'-bis-(3-hydroxy-2-benzo[b] thenylidene)hydrazine, 86% yield, mp 274-275° (from DMF). Found: C 61.01; H 3.59; S 17.30%. $C_{13}H_{12}O_2N_2S_2$. Calculated: C 61.34; H 3.43; S 18.20%. N, N'-bis-(3-hydroxy-2-benzo[b]thenylidene)-p-phenylenediamine, 99% yield, mp > 360° (decompn.) (from DMF). Found: C 66.40; H 4.13; S 14.48%. $C_{24}H_{16}O_2N_2S_2 \cdot 0.5H_2O$. Calculated: C 65.88; H 3.92; S 14.66%. N, N'-bis-(3-hydroxy-2-benzo[b]thenylidene)-butylenediamine, 93% yield, mp 237-238° (from DMF). Found: C 63.18; H 5.19; S 15.28%. $C_{22}H_{20}O_2N_2S_2$. Calculated: C 63.28; H 5.18; S 15.36%.

3-Hydroxy-2-phenyliminomethylbenzo[b]thiophene (II, $R = C_6H_5$). A mixture of 0.9 g of (I) and 5 g of aniline was heated at 80-100° for 1 h. Then the mixture was cooled, 10 ml of ethanol was added, and the obtained precipitate was filtered the next day, washed with ethanol, and dried in vacuo over P_2O_5 . We obtained 1.05 g (82%) of (II), mp 181-182.5° (from ethanol). Found: C 71.03; H 4.39; S 12.60%. C₁₅H₁₁ONS. Calculated: C 71.11; H 4.38; S 12.66%.

 $\frac{3-\text{Hydroxy}-2-(\text{p-nitrophenyliminomethyl})\text{benzo[b]thiophene (II, R = p-C_6H_4NO_2)}.$ To a solution of 3 g of (I) in 10 ml of ethanol was added a solution of 2.33 g of p-nitroaniline in 15 ml of ethanol, the mixture was refluxed for 1 h, cooled, and the precipitate was filtered, washed with alcohol, and dried. We obtained 3.8 g (76%) of (II), mp 216° (from ethanol and 80% DMF). Found: C 60.16; H 3.48; N 8.93; S 10.79%. C_{15}H_{10}O_3N_2S. Calculated: C 60.27; H 3.37; N 9.37; S 10.93%.

<u>3-Hydroxy-2-(p-carboxyphenyliminomethyl)benzo[b]thiophene (II, R = p-C₆H₄COOH).</u> Solutions of 2 g of (I) in 40 ml of methanol and 1.7 g of p-aminobenzoic acid in 30 ml of methanol were combined and heated up to the boil. Then the mixture was cooled, 70 ml of water was added, and the obtained precipitate was filtered the next day, washed with methanol, and dried. We obtained 2.92 g (87.8%) of (II), mp > 300° (de-compn.) (from methanol). Found: C 64.45; H 3.60; S 10.53%. C₁₆H₁₁O₃NS. Calculated: C 64.63; H 3.73; S 10.78%.

 $\frac{3-\text{Hydroxy}-2-(\alpha-\text{naphthylimino}(^{15}\text{N})\text{methyl)benzo[b]thiophene (II, R = \alpha-\text{naphthyl}).}{\text{To a solution of 0.45 g of (II) (R = H) in 20 ml of ethanol was added a solution of 0.36 g of <math>\alpha$ -naphthylamine(^{15}\text{N}) in 10 ml of ethanol. The mixture was evaporated to a volume of 7 ml, cooled, and the obtained yellow crystalline precipitate was filtered, washed with alcohol, then with ether, and dried in the air. We obtained 0.44 g (58%) of (II), mp 154-155°. Found: C 74.54; H 4.26; S 10.48%. C₁₉H₁₃ONS. Calculated: C 74.98; H 4.30; S 10.53%.

Preparation of Complexes (IV), (V), and (VI)

The complexes were obtained by the usual procedures, by the reaction of solutions of the ligands (I), (II) or (III) with solutions of the metal salts (MS) in ratios of (I): MS = (II): MS = 2:1 and (III): MS = 1:1, or by the reaction of amines with the chelates (V). The data on the obtained complexes are given in Table 1. As solvents we used ethanol, methanol, acetone, DMF, DMSO, etc.

CONCLUSIONS

Some new complexing compounds were obtained from 3-hydroxy-2-benzo[b]thiophenecarboxaldehyde, from which a number of new chelate compounds was obtained by reaction with metal salts.

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