CONDENSED HETEROAROMATIC SYSTEMS INCLUDING A THIOPHENE RING. XXXII.* PREPARATION AND MAGNETIC PROPERTIES OF CHELATES BASED ON 2-MERCAPTO-3-BENZO[b]FORMYLTHIOPHENE, 2-MERCAPTO-3-IMINOMETHYLBENZO[b]THIOPHENE, AND N,N'-BIS(2-MERCAPTO-3-BENZO[b]THENYLIDENE)ETHYLENEDIAMINE

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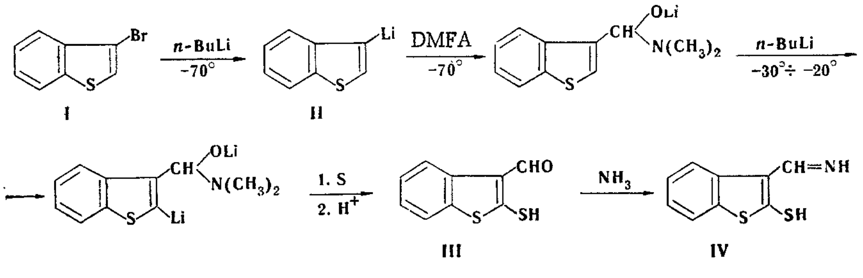
A convenient method was worked out for the preparation of 2-mercapto-3-benzo[b]formylthiophene from 3-bromobenzo[b]thiophene. 2-Mercapto-3-benzo[b]formylthiophene and Schiff bases from it react readily with metal salts to give complexes. The magnetic properties of the chelates were studied, and it was found that the dependence of the magnetic susceptibility on the temperature passes through a minimum for (2-mercapto-3-benzo[b]formylthiophenato)Co and {N,N'-bis(2-mercapto-3-benzo[b]thenylidene)ethylenediaminato}cobalt. On the basis of the magnetic susceptibility data it was concluded that the chelates have planar structures.

We have previously described [2, 3] new types of complexing compounds — mercapto aldimines of the thieno[3,2-b]thiophene and benzo[b]thiophene series — which are of considerable interest for the preparation of complexes with metal ions. The synthesis of mercapto aldimines of this class of heterocycles was carried out under the conditions described for thiophene or furan derivatives [4, 5]. i.e., by the action of sodium in liquid ammonia on the acetals of the appropriate alkylmercapto aldehydes.

A modification of the method for the introduction of two functional groups into the thiophene ring by metallation with n-butyllithium [6, 7] enables us to considerably simplify the synthesis of difunctionally substituted derivatives of the indicated condensed systems. The reaction of 3-bromobenzo[b]thiophene (I) with n-butyllithium gave 3-benzo[b]thienyllithium (II), which was treated successively with dimethylformamide (DMFA), n-butyllithium, and elementary sulfur. Hydrolysis of the mixture gives 2-mercapto-3-benzo[b]formylthiophenes (III) in 80% yields. Schiff bases are readily formed by the reaction of aldehyde III with amines. We used this method to prepare 2-mercapto-3-iminomethylbenzo[b]thiophene (IV), N,N'-bis(2- mercapto-3-benzo[b]thenylidene)ethylenediamine (VIII), 2-mercapto-3-(β-naphthyliminomethyl)benzo[b]thiophene (IX), and several other compounds.



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*See [1] for communication XXXI.

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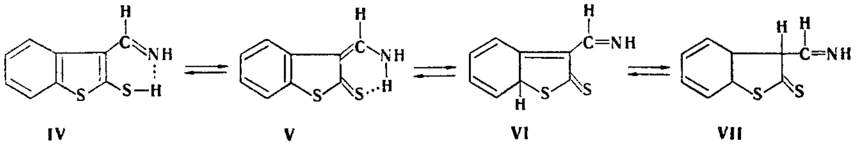
TABLE 1. Magnetic Properties of Chelates XI (M = Co and Cu) and XII (M = Co and Cu)

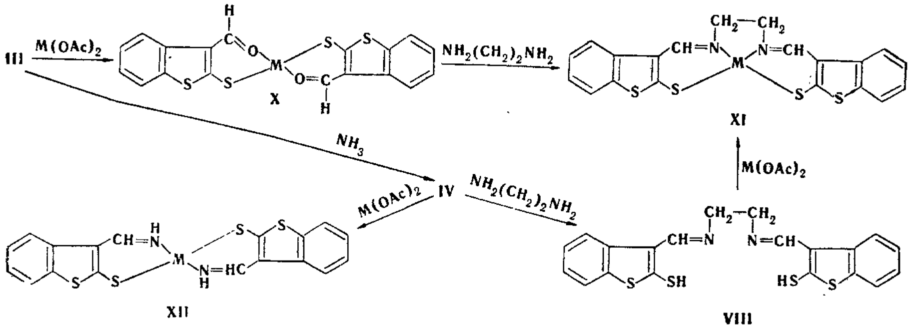
XI (M=Co)			XII (M=Co)			XI (M=Cu)			XII (M=Cu)		
T, K	$\chi' \cdot 10^6$	μ_{eff}, B.m.	T, K	$\chi' \cdot 10^6$	μ_{eff}, B.m.	T, K	$\chi' \cdot 10^6$	μ_{eff}, B.m.	T, K	$\chi' \cdot 10^6$	μ_{eff}, B.m.
407,0	529	1,39	409,5	853	1,68	269,5	1462	1,87	296,0	1198	1,69
383,0	553	1,31	379,0	809	1,57	285,0	1523	1,87	279,0	1266	1,69
352,0	499	1,19	351,0	763	1,47	267,0	1622	1,87	248,0	1428	1,69
330,0	475	1,12	328,5	740	1,40	247,0	1738	1,87	210,0	1685	1,69
300,0	417	1,00	298,5	691	1,29	219,0	1960	1,86	195,0	1835	1,70
278,5	397	0,94	271,0	652	1,19	201,0	2137	1,86	159,0	2280	1,71
251,0	367	0,85	249,0	599	1,10	191,0	2248	1,86	146,0	2485	1,71
218,5	340	0,77	214,0	514	0,94	157,0	2710	1,85	97,0	3821	1,73
191,0	332	0,72	191,0	510	0,89	115,0	3650	1,84	79,0	4837	1,76
170,0	350	0,69	168,5	538	0,86	83,0	4990	1,83			
150,0	372	0,67	145,0	560	0,81						
115,0	430	0,63	115,0	631	0,77						
79,0	601	0,62	79,0	929	0,77						

Let us note that mercapto aldimine IV is potentially capable of existing as tautomeric forms IV-VII or as an equilibrium mixture of them.



The data obtained from a study of the PMR spectra enabled us to conclude that mercapto aldimine IV exists in solution primarily in thione form V [8] (however, for convenience we will here and subsequently call compounds of this type mercapto aldimines). This sort of tautomerism is also possible for aldehyde III.

Chelates X, which on treatment with amines are converted to chelates XI, are formed in the reaction of aldehyde III with metal salts. Chelates XI are also obtained by reaction of the appropriate Schiff bases with metal salts.



M = Cu, Co, Ni, Zn

The type of ligands under consideration and complexes based on them have the properties of inhibitors of the oxidation of hydrocarbons and thermal stabilizers and photostabilizers of polyamides. In this connection, it seemed of interest to investigate their chemical and physical properties more closely. We have previously reported [9] preliminary data relating to the crystal lattice of {N,N'-bis(2-mercapto-3-benzo[b]thenylidene)ethylenediaminato}nickel (II) (XI, M = Ni). In the present paper we present the results of a study of the magnetic properties of the chelates obtained.

Complexes of the XI and XII composition (M = Co, Ni, and Cu) were investigated by the method of static magnetic susceptibility with a modernized Faraday balance, of which the schematic diagram and the method of measurement were presented in [10]. The magnetic sus-

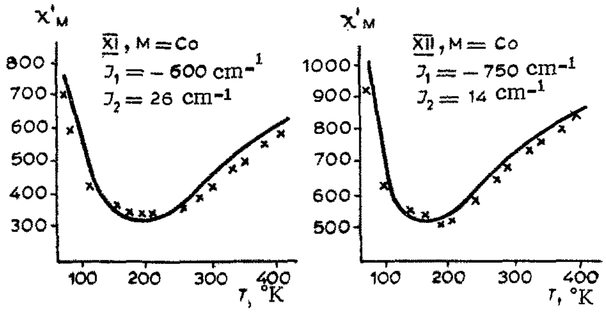


Fig. 1. Temperature dependence of χ'_M for chelates XI and XII (M = Co): theoretical curve (———); experimental curve (XXXXXX).

ceptibilities of (XI) (M = Co) and XII (M = Co) were measured at 80-400°K, whereas the magnetic susceptibilities of XI (M = Ni and Cu) and XII (M = Ni and Cu) were measured at 80-300°K. The results are presented in Table 1 and Fig. 1. The susceptibilities of copper chelates XI (M = Cu) and XII (M = Cu) obey the Curie—Weiss law $\chi = C/T + \theta$ with $\theta = 5$ and -8°K, respectively. The very slight dependence of the magnetic moment (μ_{eff}) on the temperature attests to the absence of spin—spin exchange and to the small effect of the spin—orbital interaction.

The magnetism of all of the investigated XI and XII (M = Co, Ni, and Cu) indicates their planar structure. The diamagnetism of the nickel XI (M = Ni) and XII (M = Ni) compound and the low μ_{eff} values of the cobalt XI (M = Co) and XII (M = Co) complexes constitute the principal proof for this. An unusual trend of the dependence of the magnetic susceptibility (χ) on the temperature is observed for the latter compounds. This is manifested in the fact that at ∿ 190°K the magnetic susceptibility passes through a minimum (see Fig. 1). The magnetic moments depend appreciably on the temperature. Their values at 300°K are less than the purely spin value for one unpaired electron [1.73 Bohr magneton (B.m.)] and decrease by a factor of ∿ 2 for both compounds as the temperature is lowered to 79°K.

The increase in the magnetic susceptibility for chelates XI (M = Co) and XII (M = Co) can be explained by the fact that ferromagnetic exchange can be realized along with an antiferromagnetic exchange in the investigated systems, and the fraction of each of these exchanges depends on the temperature: the ferromagnetic interaction prevails as the temperature is lowered. The formula obtained from the known Van Vleck expression with allowance for the antiferromagnetic ($J_1 < 0$) and ferromagnetic ($J_2 > 0$) exchanges for two interacting paramagnetic particles with a spin of 1/2 was used for the calculation of the dependence of χ and T:

$$\chi = \frac{1}{T}\left[\frac{1}{1+1/3e^{-J1/kT}} + \frac{1}{1+1/3e^{-J2/kT}} + 0.75\right],$$

where, to a first approximation, it is assumed that

$$N\beta^2/3k = 1/8 \text{ and } g = 2.$$

It is easy to see that when $J_1 = J_2 = 0$ the above expression is converted to the usual Curie equation for paramagnetic substances. A comparison of the experimental and theoretical data is presented in Fig. 1. The small deviations in the experimental and theoretical curves constitute evidence for a more complex dependence of the relationship between the antiferromagnetic and ferromagnetic contributions. Nevertheless, although the calculations were made within a first approximation, analysis of Fig. 1 shows the possibility of this interpretation of the temperature dependence of the magnetic susceptibility of the investigated chelates, which passes through a minimum.

TABLE 2. Properties of Chelates XI (M = Co and Ni) and XII (M = Cu, Co, Ni, and Zn)

Chelate No.	Ligand No.	mp (dec.) °C	Empirical formula	Found,					Calc., %					Chelate color	Yield, %
				C	H	N	S	M	C	H	N	S	M		
XI, M=Co	III	>310	$C_{20}H_{14}CoN_2S_4$	51,0	3,1		27,4	12,5	51,1	3,0		27,3	12,6	Black	59
	IV	>310		50,8	3,2		27,6	12,4							65
XI, M=Ni	III	>350	$C_{20}H_{14}N_2NiS_4$	51,6	3,1		27,2	12,5	51,2	3,0		27,3	12,5	Dark green	53
	IV	>350		51,2	3,3										99
XII, M=Cu	IV	>350	$C_{18}H_{12}CuN_2S_4$	47,6	2,6		28,4	13,8	48,2	2,7		28,6	14,2	Brown	90
XII, M=Co	IV	>360	$C_{18}H_{12}CoN_2S_4$	49,2	2,8		29,0		48,7	2,7		28,9		Brown	86
XII, M=Ni	IV	>360	$C_{18}H_{12}N_2NiS_4$	48,7	2,7	6,4	28,6		48,7	2,4	6,3	28,9		Black	67
XII, M=Zn	IV	305	$C_{18}H_{12}N_2S_4Zn$	48,3	2,8	5,9			48,1	2,7	6,2			Yellow	83

EXPERIMENTAL METHOD

The magnetic susceptibility was investigated with a modified Faraday balance [10]. The standard was $HgCo(NCS)_4$. The diamagnetic corrections were determined from tables [11].

2-Mercapto-3-benzo[b]formylthiophene (III). A solution of 66 g (0.35 mole) of 3-bromobenzo[b]thiophene (I) in 100 ml of absolute ether was added to a cooled (–70°C) ether solution of 19.8 g (0.31 mole) of n-butyllithium, and the mixture was stirred for 30 min at –70°. A solution of 27 g (0.37 mole) of DMFA in 60 ml of absolute ether was then added to the resulting mixture at –70°, the cooling bath was removed, and a second equivalent of n-butyllithium (19.8g) was added at –20° after 40-45 min. When the temperature of the mixture reached room temperature, it was refluxed for 30 min, cooled to –20°, and treated with 9.9 g (0.31 mole) of finely ground sulfur. The mixture was then refluxed for 1.5 h, after which it was hydrolyzed at 0°, the aqueous layer was separated, and the ether layer was washed with water. The combined water layers were acidified to pH 2 with HCl (1:1), and the liberated orange-red oil was separated and treated with hot alcohol to give 48.6 g (80%) of III, which was soluble in benzene, chloroform, DMFA, diglyme, and N,N-dimethylacetamide. Two reprecipitations from DMFA by the addition of methanol give a product with mp 172-173°. Found %: C 55.6; H 2.8; S 33.1. $C_9H_6OS_2$. Calculated %: C 55.6; H 3.1; S 33.0.

Refluxing equivalent amounts of aldehyde III and β-naphthylamine in DMFA gave 2-mercapto-3-(β-naphthyliminomethyl)-benzo[b]thiophene (IX) with mp 216=217° (from alcohol–benzene). Found %: N 4.4. $C_{19}H_{13}NS_2$. Calculated %: N 4.4. No melting-point depression was observed for a mixture of this product with IX obtained by an independent method.

Refluxing a mixture of aldehyde III, alcohol, and 25% ammonium hydroxide gave 2-mercapto-3-iminomethylbenzo[b]thiophene (IV) with mp 160-161° (from alcohol) in 70% yield. Found %: C 56.4; H 3.8; N 7.1; S 33.1. $C_9H_7NS_2$. Calculated %: C 56.9; H 3.6; N 7.2; S 33.2.

The IR spectrum of mercapto aldimine IV proved to be identical to the spectrum of the compound obtained by the action of sodium in liquid ammonia on 2-ethylmercapto-3-benzo-[b]formylthiophene acetal [2].

Reaction of aldehyde III with ethylenediamine (in a ratio of 2:1) in DMFA gave N,N'-bis(2-mercapto-3-benzo[b]thenylidene)-ethylenediamine (VIII) with mp 260-265° (after reprecipitation from DMFA by the addition of alcohol) in 82% yield. Found %: C 58.2; H 3.8; S 30.9. $C_{20}H_{16}N_2S_4$. Calculated %: C 58.2; H 3.9; S 31.1. The IR and UV spectra of VIII were identical to the spectrum of the compound obtained by reaction of ethylenediamine with mercapto aldimine IV prepared by the method in [2].

Bis(2-mercapto-3-benzo[b]formylthiophenato)copper (II) (X, M = Cu). A solution of 1 g (0.005 mole) of copper acetate in 100 ml of DMFA was added to a solution of 2 g (0.01 mole) of aldehyde III in 50 ml of DMFA, and the mixture was refluxed briefly, cooled, and diluted with methanol. The resulting brown precipitate was removed by filtration, washed thoroughly with hot methanol and ether, and vacuum dried over P_2O_5 at

140° to give 1 g (45%) of chelate X (M = Cu) with mp ∿ 205° (dec.). Found %: C 48.1; H 3.0; Cu 14.6; S 28.2. $C_{18}H_{20}CuO_2S_4$. Calculated %: C 48.0; H 2.4; Cu 14.1; S 28.5.

Bis(2-mercapto-3-benzo[b]formylthiophenato)cobalt (II) (X, M = Co), with mp > 260° (dec.), was similarly obtained in 41% yield. Found %: C 48.7; H 2.9; Co 13.5; S 29.0. $C_{18}H_{12}CoO_2S_4$. Calculated %: C 48.5; H 2.3; Co 13.2; S 28.8.

N,N'-{Bis(2-mercapto-3-benzo[b]thenylidene)ethylenediaminato}copper (II) (XI, M = Cu). A 3-g (7.3 mmole) sample of N,N'-bis(2-mercapto-3-benzo[b]thenylidene)ethylenediamine (VIII), purified by reprecipitation from DMFA by the addition of methanol or ethanol, was dissolved by heating in 250 ml of DMFA, after which the solution was filtered, and a solution of 1.45 g (7.3 mmole) of copper acetate in 100 ml of DMFA was added to it. Brown needles precipitated immediately when the solutions were mixed. The precipitate was removed by filtration, washed with alcohol and ether, and dried to give 2.9 g (84%) of chelate XI (M = Cu) with mp > 270° (dec.). Found %: C 50.6; H 3.2; Cu 13.3; S 26.7. $C_{20}H_{14}CuN_2S_4$. Calculated %: C 50.7; H 3.0; Cu 13.4; S 27.0.

Chelate XI (M = Cu) was also obtained in 91% yield by successive treatment of mercapto aldimine IV with ethylenediamine and copper acetate in DMFA, and had mp ∿ 280° (dec.). Found %: C 50.7; H 3.2; Cu 13.2; S 26.4. The IR and UV spectra of these chelates were identical.

Chelates XI (M = Co and Ni) and XII (M = Cu, Co, Ni, and Zn) were similarly obtained (See Table 2).

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