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SYNTHESIS OF ALKALI AND HEAVY METAL DITHIO- AND THIOCARBAMATES BASED ON N-(β-AMINOETHYL)PIPERAZINE

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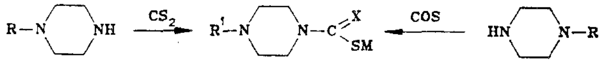
A series of alkali and heavy metal dithio- and thiocarbamates based on N-(β-aminoethyl)piperazine and its derivatives N-(β-piperazinoethyl)imides, N-[(β-2,5-dimethyl-1-pyrrolyl)ethyl]piperazine, and N-(β-salicylideneaminoethyl)-piperazine is prepared. Methods for preparation of dithio- and thiocarbamates based on piperazine are improved. Alkali metal dithio- and thiocarbamates based on piperazines form polymeric complexes with heavy metals.

Reaction of piperazines [1], including N-(β-aminoethyl)piperazine [2], and derivatives with carbon disulfide and carbonyl sulfide to prepare complexing agents and stabilizers for polymers and pesticides generates interest in the production of piperazines.

The reaction of cyclic polyamines and their derivatives with CS_2 and COS has been studied little. The reaction of piperazine Ia with carbon disulfide and NaOH leads to sodium piperazine-N,N'-bisdithiocarboxylate (IIa) [3]. Compound IIa can be prepared by reaction of piperazine Ia with CS_2 in water or alcohol with subsequent neutralization by NaOH. Under these conditions, piperazine Ia and N-(β-aminoethyl)piperazine (Ib) form the corresponding dithiocarbamates IIb-f with yields greater than 80%.



Ia,b

IIa, f; IIIa, b

Ia R=H, b R=$(CH_2)_2NH_2$; IIa–c, IIIa R^1=C(=X)SM, IId–f IIIb R^1=$(CH_2)_2NH$–C(=X)SM; IIa–f X=S, IIIa,b X=O; IIa,d IIIa,b M=Na, IIb, e M=K, c,f M=NH_4

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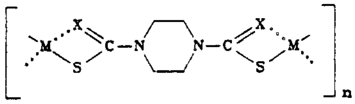
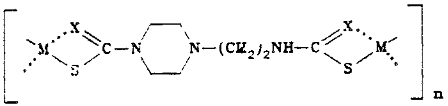
Thiocarbamates IIIa and b are unstable and are formed in low yields (40-45%). However, the yield can be raised to 60-70% by passing COS through aqueous or alcoholic solutions of Ia and b with subsequent treatment with NaOH.

The Na, K, and NH_4-dithiocarbamates IId-f based on piperazine Ib are very stable on storage. Analysis of K, Na, and NH_4-dithiocarbamates IId-g [sic] after storage for a year showed no structural changes, probably due to stabilization by piperazine Ib itself in microquantities. In each case where compound Ib was added in 0.1% to samples stored for a year, deviations from the norm were not seen.

The dithiocarbamates IIc-f can be used as flotation reagents. Thus, flotation of copper-zinc ores using IIe can increase the selectivity and extraction of zinc in the concentrate in comparison with butylxanthogenate [4]. Dithiocarbamates are very promising as stabilizers for polyvinylchloride [5, 6]. Salts and complexes of substituted dithiocarbamic acids are widely used against various fungal diseases of plants. Zinc complexes are especially effective ("Zineba" type preparations) [7, p. 230]. Thus, the synthesis of dithicarbamates XIa-g, XIIa-c, and XIIIa-c based on piperazine derivatives is interesting.

Treatment of compounds IIa-f and IIIa and b with solutions of heavy metals (Zn, Ni, Co, Mn, etc.) formed polymeric complexes IVa-i, Va-e, VIa-i, and VIIa-e.


IVa-i Va-e


VIa-i, VIIa-e

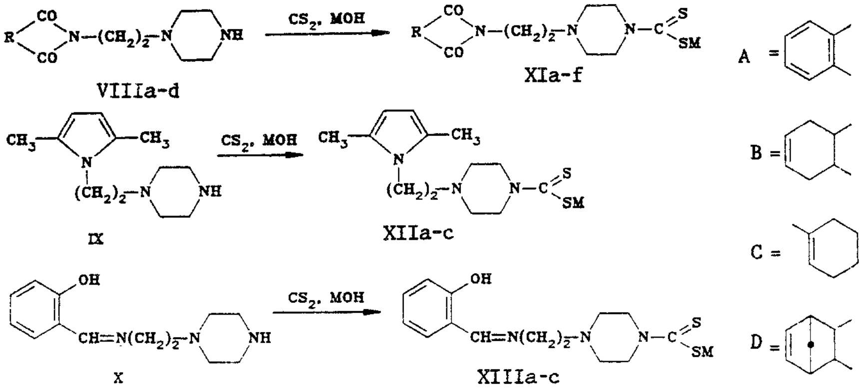
IVa-i VIa-i X=S, Va-e VIIa-e X=O; IV—VII a M=Zn, b M=Ni, c M=Co; IVd–VId M=Mn, IVe–VI e VIId M=Cu, IVf-VIf, VIIe M=Cd; IV—VI g M=Fe, h M=Sn, i M=Pb

IR spectra of dithiocarbamates IIa-f and IIIa and b have absorption bands at 1400 and 1470 cm^{-1} (N—C=S) [8, p. 507]. Absorption bands at 1480 and 1540 cm^{-1}, characteristic for stretching vibrations of shortened C—N bonds in the NCS_2M fragment [8, p. 507], appear in the IR spectra of the metal complexes Va-i and VIa-i.

The compounds N-(β-piperazinoethyl)imides VIIIa-d, N-[(β-2,5-dimethyl-1-pyrrolyl)ethyl]-piperazine (IX), and N-(β-salicylideneaminoethyl)piperazine (X) also react with CS_2. Compounds VIIIa-d, IX, and X react with CS_2 and base just as easily as Ib, forming the corresponding dithiocarbamates XIa-f, XIIa-c, and XIIIa-c with high yields.

Methods for preparation of XIa-f and XIIa-c are described in [9].

IR spectra of XIa-f have absorption bands at 1720, 1780, and 1420-1490 cm^{-1}, characteristic of the imide group in a >N—C=S structure.

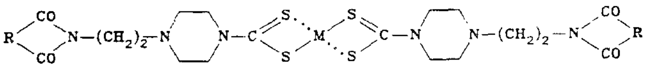


VIIIa XIa–c R=A, VIIIb XId R=B VIIIc; XIe R=C VIIId XIf R=D; VIIIa–c XIa,d,eXIIa, XIIIa M=Na VIII d XIb,f XIIb XIIIb M=K, XIc–XIIc $M=NH_4$

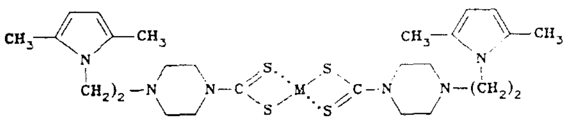
The heavy metal dithiocarbamate complexes XIVa-ℓ, XVa-c, and XVIa-d, were prepared from dithiocarbamates XIa-f-XIIIa-c. Thus, heavy metal dithiocarbamates based on derivatives of Ib with a protected amino-group were synthesized. Dithiocarbamates based on the phthalimides XIa-e, the norbornenedicarbonylimide XIf, pyrroles XIIa-c, and N-(β-salicylideneaminoethyl)-piperazine XIIIa-c were used as starting materials for synthesis of compounds XIVa-ℓ, XVa-c, XVIa-c, and the Zn, Ni, Co, Pb, Fe, and Mn complexes.

TABLE 1. Properties of Compounds II-VII and XI-XVI

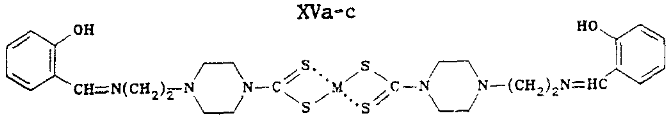
Compound	Empirical formula	mp, °C	Yield, %	Compound	Empirical formula	mp, °C	Yield, %
IIa	$C_6H_8N_2Na_2S_4$	344...346	96	XIa	$C_{15}H_{16}N_3NaO_2S_2$	208	92
IIb	$C_6H_8K_2N_2S_4$	318...320	90	XIb	$C_{15}H_{16}KN_3O_2S_2$	226...228	88
IIc	$C_6H_{16}N_4S_4$	278...280	82	XIc	$C_{15}H_{20}N_4O_2S_2$	151...152	76
IId	$C_6H_8N_2Na_2S_4$	265...266	92	XId	$C_{15}H_{20}N_3NaO_2S_2$	207	97
IIe	$C_8H_{13}K_2N_3S_4$	228	97	XIe	$C_{16}H_{22}N_3NaO_2S_2$	215	95
IIf	$C_8H_{21}N_5S_4$	162...164	82	XIf	$C_{16}H_{20}KN_3O_2S_2$	235	92
IIIa	$C_6H_8N_2Na_2O_2S_2$	340 (dec.)	58	XIIa	$C_{13}H_{20}N_3NaS_2$	173	94
IIIb	$C_6H_{13}N_3Na_2O_2S_2$	215 (dec.)	52	XIIb	$C_{13}H_{20}KN_3S_2$	197...198	87
IVa	$C_6H_8N_2S_4$	300 (dec.)	78	XIIc	$C_{13}H_{24}N_4S_2$	137...139	88
IVb	$C_6H_8CoN_2S_4$	325 (dec.)	69	XIIIa	$C_{14}H_{18}N_3NaOS_2$	165...167	85
IVc	$C_6H_8MnN_2S_4$	245	90	XIIIb	$C_{14}H_{18}KN_3OS_2$	190	90
IVd	$C_6H_8CuN_2S_4$	228...230	68	XIIIc	$C_{14}H_{22}N_4OS_2$	140...142	82
IVe	$C_6H_8CoN_2S_4$	248...249	72	XIVa	$C_{30}H_{32}N_6O_4S_4Zn$	228	96
IVf	$C_5H_8CuN_2S_4$	270...272	64	XIVb	$C_{30}H_{32}N_6NiO_4S_4$	320	95
IVg	$C_6H_8FeN_2S_4$	240...242	66	XIVc	$C_{30}H_{32}N_6O_4PbS_4$	186	92
IVh	$C_5H_8N_2S_4$	330...331	58	XIVd	$C_{30}H_{32}N_6O_4S_4Zn$	235	95
IVi	$C_6H_8N_2PbS_4$	254 (dec.)	96	XIVe	$C_{30}H_{40}N_6NiO_4S_4$	263	94
Va	$C_6H_8N_2O_2S_2Zn$	290 (dec.)	67	XIVf	$C_{30}H_{40}N_6O_4PbS_4$	150	90
Vb	$C_6H_8N_2NiO_2S_2$	140 (dec.)	53	XIVg	$C_{32}H_{44}N_6O_4S_4Zn$	240	94
Vc	$C_6H_8CoN_2O_2S_2$	158 (dec.)	69	XIVh	$C_{32}H_{44}N_6NiO_4S_4$	210	92
Vd	$C_6H_8CuN_2O_2S_2$	175 (dec.)	58	XIVi	$C_{32}H_{44}N_6O_4PbS_4$	185	90
Ve	$C_6H_8CdN_2O_2S_2$	255 (dec.)	94	XIVj	$C_{32}H_{40}N_6O_4S_4Zn$	260	94
VIa	$C_8H_{13}N_3S_4Zn$	250	92	XIVk	$C_{32}H_{44}N_6NiO_4S_4$	192	88
VIb	$C_8H_{13}N_3NiS_4$	206 (dec.)	93	XIVℓ	$C_{32}H_{40}N_6O_4PbS_4$	180	95
VIc	$C_8H_{13}CoN_3S_4$	290 (dec.)	89	XVa	$C_{26}H_{40}N_6S_4Zn$	275	97
VId	$C_8H_{13}MnN_3S_4$	270 (dec.)	96	XVb	$C_{26}H_{40}N_6NiS_4$	270	98
VIe	$C_8H_{13}CuN_3S_4$	184 (dec.)	98	XVc	$C_{26}H_{40}CoN_6S_4$	240	95
VIf	$C_8H_{13}CdN_3S_4$	240 (subl.)	87	XVIa	$C_{28}H_{36}N_6O_2S_4Zn$	217	95
VIg	$C_8H_{13}FeN_3S_4$	250 (dec.)	86	XVIb	$C_{28}H_{36}CoN_6O_2S_4$	242	94
VIh	$C_8H_{13}N_3S_4Sn$	220 (dec.)	82	XVIc	$C_{28}H_{36}MnN_6O_2S_4$	252	94
VIi	$C_8H_{13}N_3PbS_4$	180 (dec.)	74	XVId	$C_{28}H_{36}FeN_6O_2S_4$	178	89
VIIa	$C_8H_{13}N_3O_2S_2Zn$	252 (dec.)	86				
VIIb	$C_8H_{13}N_3NiO_2S_2$	190 (dec.)	72				
VIIc	$C_8H_{13}CoN_3O_2S_2$	310 (subl.)	55				
VIId	$C_8H_{13}CuN_3O_2S_2$	129 (dec.)	62				
VIIe	$C_8H_{13}CdN_3O_2S_2$	185 (dec.)	78				



XIVa-ℓ



XVa-c



XVIa-d

XIVa–c R=A, d–f R=B, g–i R=C; a,d,g,j M=Zn, b,e,h,k M=Ni, c,f,i,ℓ M=Pb
XVa M=Zn, b M=Ni, c M=Co; XVI a M=Zn, b M=Co, c M=Mn, d M=Fe

EXPERIMENTAL

IR spectra were recorded on a UR-20 instrument as KBr pellets. Piperazine Ia was purified by recrystallization from a 1:1 mixture of alcohol—ether. The purity of Ia was 99.4% (GC). Chromatography was performed on a LKhM-72 instrument at 150-250°C with a helium carrier gas flow of 1.8-2.6 liter/h, a 5 m column filled with fluoropolymer-4, and a stationary phase of silicone elastomer SKTFT-50Kh.

Properties of compounds synthesized are given in Table 1. Elemental analyses of compounds II-VII for C, H, N, S, and M; compounds XI and XII for N and S; and compounds XIV-XVI for C, H, N, and S correspond to the calculated values.

N-(β-Aminoethyl)piperazine (Ib) was prepared by fractionation of a mixture of polyethylenepolyamines, a side product of ethylenediamine production, with a purity of 99.2% (GC) and bp of 217-218°C.

N-(β-Piperazinoethyl)imides VIIIa-d were prepared by condensation of Ib with anhydrides of dicarboxylic acids according to [9].

N-[(β-2,5-Dimethyl-1-pyrrolyl)ethyl]piperazine (IX, $C_{12}H_{21}N_3$). A mixture of 12.9 g (0.1 mole) Ib and 11.4 g (0.1 mole) acetonylacetone was heated at 150°C for 5 min and then vacuum distilled to give IX. Yield 19.3 g (93%), mp 12°C, bp 178-180°C (22.66 Pa), n_D^{20} 1.5298. IR spectrum: 750 cm^{-1} (pyrrole).

N-(β-Salicylideneaminoethyl)piperazine (X) was prepared by the method of [10].

Sodium Piperazine-N,N'-bisdithiocarboxylate (IIa). To a solution of 8.6 g piperazine Ia in 50 ml methanol were added dropwise 15.2 g (0.2 mole) CS_2 at room temperature and then 8 g (0.2 mole) NaOH in 25 ml methanol. The product was recrystallized from a 1:2 mixture of alcohol—acetone.

Compounds IIb and c were prepared analogously.

Alkali Metal N-(β-Aminoethyl)piperazine-N,N'-bisdithiocarboxylates (IId-f). To a solution of 12.9 g (0.1 mole) Ib and 8g (0.2 mole) NaOH in 50 ml alcohol were added dropwise at room temperature 15.2 g (0.2 mole) CS_2. The mixture was heated at 60°C for 1.5 h. The product was crystallized from a 1:2 mixture of alcohol—acetone.

Compounds IId and f were prepared analogously.

Sodium Piperazine-N,N'-bisthiocarboxylate (IIIa). Carbonyl sulfide was passed through a solution of 8.6 g (0.1 mole) piperazine Ia in 50 ml ethanol at room temperature. The quantity of added COS was measured by mass. The reaction mixture was treated with 8 g (0.2 mole) NaOH. The product was crystallized from acetone.

Compound IIIb was prepared analogously.

Metal Complexes of Piperazines IVa-i, Va-e, VIa-i, and VIIa-e. Equimolar quantities of compounds IIa-f and IIIa and b and heavy metal salts (Zn, Ni, Co, Mn, Cu, Cd, Sn, Fe, and Pb) dissolved in water were heated to 50°C for 30 min. The precipitated metal complexes were washed with distilled water until a test for salts was negative. Compounds IVa-i, Va-e, VIa-i, and VIIa-e were dried at 100°C in a stream of nitrogen.

Alkali Metal (Ammonium) Dithiocarbamates XIa-f Based on N-(β-Piperazinoethyl)imides VIIIa-d. A mixture of equimolar quantities of imides VIIIa-d, base, and CS_2 in ethanol was boiled for 1.5 h on a water bath. Compounds XIa-f were crystallized from acetone.

Alkali Metal (Ammonium) Dithiocarbamates XIIa-c Based on N-[(β-2,5-Dimethyl-1-pyrrolyl)-ethyl]piperazine (IX). A mixture of equimolar quantities of pyrrole IX, base, and CS_2 in ethanol was boiled for 20 min. Products XIIa-c were isolated by crystallization from a 1:2 mixture of alcohol—acetone.

Alkali Metal (Ammonium) Dithiocarbamates XIIIa-c Based on N-(β-Salicylideneaminoethyl)piperazine (X). A mixture of equimolar quantities of compound X, base, and CS_2 in water was heated to 60°C for 40 min. The products were crystallized from a 1:1 mixture of alcohol—acetone.

Heavy Metal Dithiocarbamates XIVa-ℓ, XVa-c, and XVIa-d Based on N-(β-Piperazinoethyl)-imides, N-[(β-2,5-Dimethyl-1-pyrrolyl)ethyl]piperazine, and N-(β-Salicylideneaminoethyl)-piperazine. A mixture of 0.1 mole of compounds XIa-f in 100 ml distilled water and 0.05 mole of aqueous Zn, Ni, or Pb salt was stirred at 50°C for 30 min. The precipitate was washed with distilled water until complete removal of alkali metal or ammonium salt and then dried at 110°C in a stream of nitrogen. Metal complexes XVa-c and XVIa-d were prepared analogously using water-soluble salts of Zn, Ni, Co, Pb, Mn, and Fe. Yields were 88-100%.

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