# ՀԱՅԱՍՏԱՆԻ ՀԱՆՐԱՊԵՏՈՒԹՅԱՆ ԳԻՏՈՒԹՅՈՒՆՆԵՐԻ ԱՉԳԱՅԻՆ ԱԿԱԴԵՍԻԱ НАЦИОНАЛЬНАЯ АКАДЕМИЯ НАУК РЕСПУБЛИКИ АРМЕНИЯ NATIONAL ACADEMY OF SCIENCES OF THE REPUBLIC OF ARMENIA

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# DITHIOMALONDIAMIDES AS VERSATILE REAGENTS FOR THE SYNTHESIS OF HETEROCYCLES AND COORDINATION COMPOUNDS

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This review presents the data on the general synthetic methods for dithiomalondiamides with the focus on the chemistry of dithiomalondianilide. This work is based on a conference paper "Active methylene thioamides and selenoamides as versatile building blocks in heterocyclic chemistry" presented at «New Emerging Trends in Chemistry» Conference (NewTrendsChem-2023) (September 24-28, 2023, Yerevan, Armenia).

### 1. Introduction

Active methylene thioamides are routinely used for synthesis of various functionalized N,S-heterocycles such as 2-mercapto(2-thioxo)pyridines [1–6], 4H-thiopyrans [7,8] and thiochromones [9], thiazolines [10], isothiazoles [11,12], 1,2,4-dithiazoles [13], 1,2,3-thiadiazoles and 1,2,3-triazoles [14,15], thieno[2,3-b]pyridines [16–21], 1,3,5-thiadiazines [22,23] many of which are shown to be promising organic semi-conductors, fluorescent dyes, drugs, agrochemicals etc.

While the chemistry of cyanothioacetamide NCCH<sub>2</sub>C(S)NH<sub>2</sub> [24–27] and  $\beta$ -ketothioamides [27,28] is quite well developed, less attention has been paid to the chemistry of active methylene thio- and dithiomalonamides despite the fact that the latter show often quite different behavior resulting in unique products. Thus, the chemistry of the readily available dithiomalon-dianilide (N,N'-diphenyldithiomalondiamide) is considered in only a few dozen papers. The aim of this microreview is to popularize the chemistry of

these reagents and to demonstrate the synthetic potential of dithiomalonamides.

## 2. General approaches to preparation of dithiomalonamides

One of the most obvious approaches to the synthesis of dithiomalondianilides is based on the action of tetraphosphorus decasulfide ( $P_4S_{10}$ ) on N,N'-diphenylmalonamide **2** in anhydrous solvents such as dioxane or toluene (schem. 1) [29].

Scheme 1



N,N'-Diphenyldithiomalonamide **1** is a yellow powder (m.p. $150-152^{\circ}C$ ), readily soluble in acetone, DMF, ethyl acetate, DMSO, sparingly soluble in ethanol, insoluble in water and ethers [30].

Upon treatment with  $P_4S_{10}$  in dioxane, diazomalondiamide **3** undergo transformation to the unsubstituted dithiomalonamide **4** [31] (schem. 2). However, it is obvious that this approach is not effective and cannot be used for the large-scale synthesis of dithiomalonamides.

Scheme 2



Lawesson's reagent (2,4-bis-(4-methoxyphenyl)-1,3-dithiadiphosphetane-2,4-dithione) (LR) is a more effective thiating reagent superioir to  $P_4S_{10}$ [32]. Dithiomalonanilide **1** can be prepared by theatment of the corresponding amide **2** with LR in hexamethylphosphortriamide (HMPA) at 80-100°*C* (schem. 3) [33].

Scheme 3



A better approach to the preparation of unsubstituted dithiomalonamide **4** is based on the reaction of hydrogen sulfide with malononitrile **5**. The reaction readily occurs in absolute ethanol at  $-10^{\circ}C$  and catalyzed by potassium ethoxide formed *in situ* from potassium metal and cold EtOH (schem. 4) [34].

Scheme 4



In a similar way, substituted dithiomalonamides 7 can be prepared using substituted malononitriles 6. The synthesis is carried out at room temperature and catalyzed with potassium ethoxide. The reaction mixture was treated with hydrogen sulfide at elevated pressure (schem. 5) [35].

Scheme 5





Also, the method based on the treatment of arylamines **8** with carbon subsulfide  $C_3S_2$  useful for preparation dithiomalonamides **9** was described in the early literature [9] (schem. 6). However, this method is used quite rarely due to the instability of  $C_3S_2$  and low yields of the products.

Scheme 6



The best and most handy approach to the preparation of dithiomalonic acid diarylamides **9** includes the reaction aryl isothiocyanates with sodium acetylacetonate **11**. The latter can be prepared *in situ* by dissolving acetylacetone **10** in absolute ether followed by treatment with sodium metal dust (schem. 7). The yields of the products **9** in this reaction are almost quantitative [10]. 392



Dithiomalonamide **4** can be prepared by the recyclization of 4-aryl-2,6diamino-4H-thiopyran-3,5-dicarbonitriles **12** upon treatment with hydrogen sulfide in pyridine in the presence of  $Et_3N$ . The yields vary in the range of 70-79%, though the method cannot be considered as atom-economic (scheme 8) [38].

Scheme 8



The paper [39] describes a method for preparation of dithiomalonic acid dimorpholide **18**. The starting substrate is dithioacetic acid **13**, which was treated with strong bases such as butyl lithium or LDA to form dianion **14**. When treated with  $CS_2$  at 20 °C this dianion afforded tetrathiomalonic acid trianion **15**. The latter via tetraanion **16** and dithiethane **17** gave dithiomalonic acid dimorpholide **18** (schem. 9).



### 3. The reactions of dithiomalonamides

## 3.1. Preparation of 1,2-dithiol derivatives

As it was shown in the paper [40], dithiomalondianilide **9** can be easily oxidized to form cyclization products, 1,2-dithiols. Dithiols were found to react esily with alkali or acids, reducing agents, hydrazine, bromine to give a couple of heterocyclic products **19-24** (schem. 10).



 $Ar = Ph, 4-MeC_6H_4.$ 

The oxidation of dithiomalonamides **9** to 1,2-dithiols **25** can be initiated with thionyl chloride [41] (schem. 11).

Scheme 11



The products of Knoevenagel condensation of aldehydes with dithiomalondiamides **9**, e.g. compounds **26**, under similar conditions also react to provide functionalized 1,2-dithiols **27** [41] (schem. 12).

Scheme 12



The reaction of dithiomalonamide **4** with aryl diazonium salts was reported [42]. As a result, arylhydrazones of dithiomesoxalic acid diamides **28** were formed in good yields. The oxidation with bromine in chloroform leads to the formation of 4-arylazo-1,2-dithiolium bromides **29** (schem. 13). Compounds **28** are of special interest due to antimicrobial, pesticide and fungicidal activity of close analogs [43].

Scheme 13



When reacted with iodine, dithiomalonamide **9** undergo oxidation reaction to afford 1,2-dithiols **30** (schem. 14) [44]:

Scheme 14



Dithiomalonamides **31** undergo oxidation by hydrogen peroxide in the presence of strong acids HX (X = Cl, Br), or FeBr<sub>3</sub>×6H<sub>2</sub>O and Fe[ClO<sub>4</sub>]<sub>3</sub>×6H<sub>2</sub>O in aqueous solution to give pseudoaromatic salts **32** (schem.15) [45, 46].

Scheme 15

$$R \xrightarrow{H} X \xrightarrow{H} N \xrightarrow{R} R \xrightarrow{HX, H_2O_2, Fe^{3+}} R \xrightarrow{X} H_{N, R} \xrightarrow{R = H, Me} R \xrightarrow{K} H_{N, R} \xrightarrow{X} R \xrightarrow{X} R$$

1,2-Ditiolium salt **35** was prepared by the reaction of tin(IV) chloride **33** with N,N'-diethyl dithiomalondiamide **34** [47] (schem. 16). The product was purified by recrystallization from benzene.

Scheme 16



Earlier we found that dithiomalondianilide **1** reacts with arylidene malononitriles in the presence of morpholine in hot EtOH to give [1,2]dithiolo[3,4-b]pyridine-5-carbonitriles **36** [48]. Further studies showed that dithiomalondianilide **1** reacts with 3-aryl-2-cyanoacrylates [49] and

3-aryl-2-cyanoacrylamides [50,51] to give similar [1,2]dithiolo[3,4-b]pyridine-5-carbonitriles **37,38** in moderate yields (schem. 17). Dithiomalondianilide **1** reacts with arylidene Meldrum's acids (or, in three-component one-pot manner, with aromatic aldehydes and Meldrum's acid) to afford stable Michael adducts **39** [52,53]. Upon long term heating, adducts **39** undergo cyclization with simultaneous partial oxidation to result in a complex mixtures consisting of adducts **39**, pyridine-2-thiolates **41** and tetrahydrodithiolopyridines **40** [52].



3.2. Synthesis of thiazoles

Dithiomalondianilides **9** reacts with ethyl chloroacetate in the presence of sodium acetate to form thiazolidinones **42** in 30-55% yields. The reaction proceeds as the Hantzsch-type thiazole cyclization (schem. 18) [54].

Scheme 18

 $Ar \xrightarrow{H}_{S} \xrightarrow{S}_{g} \xrightarrow{CICH_{2}CO_{2}Et, AcONa} \xrightarrow{Ar}_{O} \xrightarrow{H}_{S} \xrightarrow{H}_{Ar} 42$ 

When heated with  $\omega$ -bromoacetophenone, dithiomalondianilide **1** gives 3,3-diaryl-1,4,4-diphenyl-2-methylenedithiazole monobromide **43** regardless of the ratio of the reagents used (schem. 19) [55].



Unsubstituted dithiomalonamide **4** and N-monosubstituted analogs react with dialkyl acetylenedicarboxylates to provide thiazoles **44** [41] (schem. 20):

Scheme 20



At the same time, N,N'-disubstituted dithiomalonamides **9** react either with acetylenedicarboxylic acid in ethanol, or dimethyl acetylenedicarboxylate (DMAD) in acetone at only one thioamide fragment to give thiazolidin-4-ones **45** (schem. 21). The reaction proceeds smoothly at  $0 \,^{\circ}C$  at elevated temperatures resinification was observed [41].

Scheme 21



The reaction of dithiomalonamide **4** with  $\alpha$ -bromo-4-acetyl-2,6-di-*tert*butylphenol **46** in methanol afforded 2,2'-methylene-bis-4-(3",5"-di-*tert*butyl-4"-hydroxyphenyl)thiazole **47** (schem. 22). The resulting product can be used as a polymer stabilizer [56].



### 3.3. Synthesis of 1,3-dithiine derivatives

Both dithiomalonamide 4 and dithiomalondianilide 1 readily react with benzoyl- and thenoyl-2-acetylenes 48 in acidic medium to form the products of formal double S,S-Michael addition – 1,3-dithiin-6-iminium perchlorates 49 (schem. 23). The synthesis proceeds in glacial acetic acid at 20 C in the presence of an equimolar amount of HClO<sub>4</sub>. Authors claimed that in the absence of perchloric acid unidentified compounds are formed [57]. Presumably, the reaction proceeds through the formation of intermediate keto vinyl sulfide 50 due to S-nucleophilic Michael-type attack of thioamide mercaptoimine tautomer on the electron-deficient  $\beta$ -carbon atom of the starting activated acetylenes 48. Dithiomalonamide 4 and dianilide 1 form 1,3-dithiines 51 by reaction with substituted acetylene ketones 52 in glacial AcOH at 90 C in the presence of HClO<sub>4</sub> (schem. 23) [58,59]. The mechanism seems to be similar to the one described above.

Scheme 23



As it was reported [60], dithiomalondianilide **1** reacts with methyl propiolate **53** in AcOH at 65  $\mathcal{C}$  in the presence of perchloric acid to form 4-anilino-2methoxycarbonylmethyl-1,3-dithiin-6-phenyliminium perchlorate **54** in 42% yield and dithiomalonamide perchlorate **55** in 27% yield (schem. 24).

Scheme 24



Noteworthy that 1,3-dithiine **54** could not be prepared by heating dithiomalonamide perchlorate **55** with methyl propiolate **53**. Perchloric acid's role in crucial as a catalyst for this reaction:  $HClO_4$  protonates methyl

propiolate molecule **53** thereby increasing the partial positive charge on acetylene carbon atom to increase its electrophilicity which promotes significantly further reaction with S-nucleophile – dithiomalonedianilide **1**. In the absence of perchloric acid, the reaction of dithiomalondianilide **1** and methyl propiolate **53** proceeds with the formation of 4-anilino-2-metho-xycarbonylmethyl-6-phenylimino-1,3-dithiine **56** but in very low yield, up to 5% (schem. 25) [60].

Scheme 25



The authors of the paper [61] reported that the reactions of dithiomalonamide **4** or dithiomalonic acid dianilide **1** with 1-bromo-2-benzoyl- and 1-bromo-2-(2-thenoyl)acetylenes **57** in acetone or acetic acid resulted in the formation of 6-amino(anilino)-2-(2-oxo-2-phenylethylidene)-1,3-dithiin-4-iminium(phenyliminium) bromides **58**. Upon treatment with an aqueous ammonia solution, 1,3-dithiine salts **58** released free 1,3-dithiine base **59** (schem. 26).





3.4. Other reactions of dithiomalonamides

The Guareschi-Thorpe-type synthesis of 3-thioxo-2,3,5,6,7,8-hexahydroisoquinoline-4-carbonitriles **63** starting from dithiomalondiamide **4** and enamino ketone **60** was reported in the paper [62] (schem. 27). At the first stage, nucleophilic substitution of morpholine fragment occurs to give intermediate **61**. Next, after intramolecular dehydration resulted in the formation of isoquinoline-4-thiocarboxamide **62**, elimination of hydrogen sulfide from the thiocarbamoyl group occurs to give nitriles **63**. The structure of the products **63** was confirmed by IR spectroscopy and NMR spectroscopy data.



A.R. Katritzky reported [63] the reaction of dithiomalonamide **4** with 2,3-dichloro-1,4-naphthoquinone **64** leading to 1,2-*bis*(4,9-dioxo-naphtho[2,3-d]thiazol-2-yl)methane **65**. Compounds **65** are promising starting molecules for preparation of new quinone dyes. As it was reported, the reaction proceeds smoothly in EtOH in the presence of potassium carbonate (schem. 28). The structure of the product was proven using NMR spectroscopy [63].



The only isolated product of the reaction of dithiomalonamide **4** with benzoyl acetylene **66** was reported to be 3,3'-dithiobis-1-phenylprop-2-en-1one **67** [64]. The reaction proceeds in  $Et_2O$  in the presence of  $Et_3N$  in 39% yield (schem. 29). The structure of this product was confirmed by IR spectroscopy and NMR spectroscopy.

When benzenesulfonyl azide **68** reacts with dithiomalonamide **4** or dithiomalondianilide **1**, 5-amino-1,2,3-thiadiazole-4-carbothioamides **69,70** are formed in good yields. The reaction proceeds in the presence of sodium ethoxide (schem. 30). The structure of the products was proven using IR spectroscopy, NMR spectroscopy and mass spectrometry data [65]. In the case of unsymmetrically substituted dithiomalonamides, isomeric 1,2,3-thiadiazoles are formed.

Scheme 30



# $R^1 = H$ , Ph; $R^2 = H$ , Me, Ph.

In contrast to compound 1, N,N'-dialkyl substituted dithiomalonamides 9 react with DMAD to form 3-oxothien-2(3H)-ylidene derivatives 71. The reaction presumably proceeds through the formation of an intermediate 72. Intramolecular hydrogen bonds in the intermediate 72 favors further condensation (schem. 31). According to X-ray diffraction data, the product has a flat structure that can be explained by intramolecular hydrogen bonds and weak interatomic interactions between heteroatoms [66].



Dithiomalonamides **9** are good starting molecules for the synthesis of valuable 3,5-bis(arylamino)pyrazoles **73**. Thus, when treated with hydrazine in hot EtOH, N,N'-substituted dithiomalonamides form desired pyrazoles in good yields (schem. 32) [35].

Scheme 32



(1-Amino-3-(morpholin-1-yl)-1,3-propanedithione) **74**, prepared by the treatment of cyanothioacetamide **75** with two-fold excess of morpholine, was reported to be a good starting platform for the preparation of a couple of heterocycles [68] (schem. 33).

Scheme 33



As an active methylene compound, thioamide **74** reacts under Knoevenagel conditions with cinnamaldehyde to give compound **76**. Alkylation with MeI leads to enamino thiomorpholide **77**. Thiazoles **78** and **79** were prepared by reaction with active  $\alpha$ -halo carbonyls [68]. The structure of the new products was proven by means of mass spectrometry, IR and NMR spectroscopy.

The reaction of N,N,N',N'-tetrasubstituted dithiomalonamides **18,80** with carbon disulfide and sodium hydride occurs at active methylene group and leads to the formation of sodium dithiocarboxylates **81-82**. The latter 402

upon treatment with either 1,2-dibromoethane or iodomethane afforded methylene dithiomalonamides **83** (schem. 34) [69].



3.5. Complex compounds based on dithiomalondiamides

Acting as bidentate ligands, dithiomalonamide and its derivatives can form complex compounds with many transition metals. Many of the resulting complexes have similar properties. They are diamagnetic and can be neutral or cationic. Cationic complexes have a flat square configuration around the complexing metal, which is confirmed by electron spectroscopy data [70]. The structural formula of the square-type complex cation is presented in schem. 35.

Scheme 35



M = Pd, Ni, Mo, etc.

In strongly acidic media, only sulfur atoms act as coordination centers. Strong polarity of thiocarbonyl group, delocalization of electrons due to conjugation and the "softness" of complexing metals – for example, Pd (II) and Pt (II) – strongly favor the S-coordination. The S,S-coordination of dithiomalonamide complexes was confirmed by X-ray diffraction data.

In cationic complexes, the exact location of the counterions has not been determined, but according to IR spectroscopy data, one can assume that the counter ions form hydrogen bonds with amino groups of the complex cation, and the amino groups have a partial ammonium character [70].

With nickel cations, dithiomalonamide **4** (HL = Hdtma) and diphenyldithiomalonamide **1** (HL = Hdpma) form: diamagnetic flat red complexes Ni(dtma)<sub>2</sub>, Ni(dpma)<sub>2</sub>, Ni(Hdtma)<sub>2</sub>X<sub>2</sub>, where X = Cl, Br, I, ClO<sub>4</sub>, and also Ni(Hdpma)<sub>2</sub>X<sub>2</sub>, where X = I or ClO; paramagnetic octahedral green complexes Ni(Hdpma)<sub>3</sub>X<sub>2</sub>, where X = Cl, Br or ClO<sub>4</sub> and paramagnetic complexes, presumably [Ni(HL)<sub>2</sub>][NiX<sub>4</sub>] (X = Br, I), containing a planar cation and a tetrahedral anion. NiL<sub>2</sub> complexes were prepared by reacting the ligand and nickel acetate dissolved in ethanol or DMF at 5  $\mathcal{C}$  The NiL<sub>2</sub>X<sub>2</sub> and NiL<sub>3</sub>X<sub>2</sub> complexes are prepared similarly, adding the corresponding acid HX dissolved in HOAc or EtOH (X = Cl, Br, I, ClO<sub>4</sub>) to the reaction mixture. The cationic red complex [Ni(HL)<sub>2</sub>]Cl<sub>2</sub> is capable to transform into green complex [Ni(HL)<sub>2</sub>Cl<sub>2</sub>] in the solid state; the transformation occurs in moist air, whereas in a vacuum or dry atmosphere this process does not occur [71, 72].

Different types of palladium complexes can be prepared as follows:

- PdL<sub>2</sub>, where L is the dtma (dithiomalonamide 4) or dpma (dithiomalondianilide 1) ligand, is prepared by reacting palladium hydroxide Pd(OH)<sub>2</sub> with the ligand dissolved in AcOH in a molar ratio of 1:2.
- 2.  $PdL_2 \times 2DMF$  is prepared by adding diethyl ether to a solution of the  $PdL_2$  complex in dimethylformamide.
- 3.  $Pd(HL)_2X_2$  and  $PdHLX_2$ , where X = Cl, Br, I,  $ClO_4$ , were prepared by reaction of  $PdX_2$  or  $Pd(OH)_2$  in ethanol or aqueous ethanol with a ligand in the presence of HX.

Complexes of palladium with dithiomalonamides differ in stoichiometry depending on the medium from which they were isolated. Internal  $PdL_2$  complexes were isolated from glacial acetic acid. Cationic  $Pd(HL)_2X_2$  and neutral  $PdHLX_2$  complexes were isolated from strongly acidic media, in which the undissociated form of the ligand predominates. All the isolated complexes are diamagnetic. They are insoluble in non-polar solvents; internal complexes are soluble in polar solvents such as DMF, 2-metho-xyethanol (methyl cellosolve) or ethanol to reach the concentration being  $10^{-3}$  M; cationic and neutral complexes are soluble only in DMF [73, 74].

Zinc complexes were prepared by mixing a warm solution of zinc salt  $ZnX_2$ , where X = Cl, Br, I,  $ClO_4$ , with a warm solution of a ligand (Hdtma, HMe<sub>2</sub>dtma, HPh<sub>2</sub>dtma) in EtOH or AcOH. According to IR spectroscopy data, Zn complexes such as Zn(Hdtma)X<sub>2</sub> and Zn(HPh<sub>2</sub>dtma)X<sub>2</sub> have S,S-type of coordination, while complexes Zn(HMe<sub>2</sub>dtma)X<sub>2</sub> have an S,N-configuration. It was explained by the positive inductive effects of methyl groups, which increases the electron density on nitrogen atoms [75].

The platinum dithiomalonamide complex  $Pt(Hdtma)_2$  was prepared by adding a warm aqueous solution of sodium tetrachloroplatinate (II) to a hot aqueous solution of dithiomalonamide and sodium acetate trihydrate [76].

Silver complexes were prepared by mixing warm solutions of a ligand HL (HL = Hdtma, HMe<sub>2</sub>dtma, HPh<sub>2</sub>dtma) and a silver salt containing a 404

certain amount of the corresponding strong acid [77]. Thus, AgHLX complexes (X = Cl, Br, I) were prepared by reacting silver acetate AgOAc in aqueous AcOH with a ligand HL dissolved in AcOH with the addition of the corresponding acid HX. Another type of silver complexes,  $Ag(HL)_3X_2$  (X = ClO<sub>4</sub>, BH<sub>4</sub>), were prepared by reacting the ligand HL in AcOH with an aqueous solution of silver acetate AgOAc with the addition of the corresponding strong acid HX [77].

Copper complexes were prepared in a similar way:

- 1. Cu complexes HdtmaX (X=Cl, Br, I, ClO<sub>4</sub>) are formed by the reaction of copper (I) oxide  $Cu_2O$  dissolved in the corresponding acid HX and a solution of the Hdtma ligand in AcOH [77]. All the complexes of this type are soluble in DMF; the perchlorate complex is also soluble in methyl cellosolve and methanol.
- 2. Complexes  $Cu(HMe_2dtma)_2X$  (X = Cl, Br, I, ClO<sub>4</sub>) were prepared by reacting an EtOH solution of copper (I) oxide  $Cu_2O$  with the addition of HX and a solution of the ligand HMe<sub>2</sub>dtma in AcOH. These complexes are soluble in DMF; the perchlorate complex is also soluble in methyl cellosolve, methanol, nitrobenzene and acetone.
- 3. Complexes  $Cu(HPh_2dtma)_2X$  (X = Cl, Br, I) were isolated by adding copper oxide (I)  $Cu_2O$  to a solution HPh<sub>2</sub>dtma in EtOH, containing the corresponding acid HX. The compounds are soluble in DMF; the bromide complex is also soluble in methyl cellosolve and chloroform.

According to IR spectroscopy data, the complexes of Ag(I) and Cu(I) have an S,N-configuration and are electrolytes [77].

Interesting methods for preparation of Cu(II) complexes using template synthesis were described in the papers [78, 79]. In the classical method of Cu(II) complex compounds synthesis, only the complex with S,S-coordination **84** was isolated when dithiomalonamide **4** was taken as a ligand (schem. 36).

Scheme 36



However, any attempts to isolate S,N-complexes failed under usual conditions, since at low temperatures the reaction is too slow but with increasing temperature the formation turns out to be thermodynamically prohibitted. The authors [78, 79] succeeded to prepare S,N-complexes **85** using template synthesis approach with gelatin-immobilized matrix implants based on hexacyanoferrates (II) of various p-, d- and f-elements (MHF-GIM). A copper ion Cu<sup>2+</sup> acts as the template and carbonyl compounds, for example, formaldehyde, were used as auxiliary reagents that "cross-link" the resulting metallocycle (scheme 37). The structure of the complex compounds was confirmed using IR spectroscopy and mass spectrometry data.

Scheme 37



As it was shown in the dissertation [80], similar complexes **86** of dithiomalonamide **4** with the S,N-coordination pattern can be prepared with nickel usiang diacetyl as an auxiliary reagent (scheme 38). When attempting to perform the template synthesis in a gelatin-immobilized matrix based on nickel (II) hexacyanoferrate, the reaction does not proceed.

Scheme 38



Antimony and bismuth form trihalide complexes with dithiomalonamide **4**, N,N'-dimethyl- and N,N'-diphenyldithiomalonamide **1**: LMX<sub>3</sub>, where L = Hdtma, HMe<sub>2</sub>dtma, HPh<sub>2</sub>dtma; M = Sb, Bi; X = Cl, Br, I. The reaction occurs in dichloromethane with the addition of a small amount of acetone. Complexes of this type are neutral and have S,S-configuration; their structure was proven using IR spectroscopy and mass spectrometry data [81].

## 4. Biological activity and practical use of dithiomalonamides

Some complex compounds containing dithiomalonamide **4** and its derivatives as ligands were used as fungicides against such common fungal infections as botrysis gray caused by *Botrýtis cinérea* and downy mildew of grapes [82]. Substituted dithiomalonamides are quite effective corrosion inhibitors for AISI 304SS stainless steel. The corrosion inhibition effects was determined at various concentrations in a  $H_3PO_4$ -HCl mixture at 25  $^{\circ}C$  using a potentiostatic method. The most effective inhibitor is 1,5-di-*p*-methylphenyl-2,4-dithiomalonamide [83]. Dithiomalonamide complexes

containing trivalent and tetravalent manganese, as well as *bis*(1,5-diaryl-2,4-dithiomalonamido)-dioxomolybdenum (VI) complexes, can be used as corrosion inhibitors, rust and oxidation inhibitors [84,85].

Dithiomalondianilide **1** is useful reagent for accurate and selective gravimetric determination of cobalt and nickel [30]. N,N'-dimethyl-N,N'-diphenyl-dithiomalonamide and N,N'-dimethyl-N,N'-dicyclohexyldithiomalonamide are effective agents for extraction of silver Ag(I) from aqueous chloride phases. However, the use of these reagents has a limitation – they are non-selective with respect to Ag (I) if Cu (II) and Fe (III) are present in a solution [86].

The addition of N,N'-disubstituted dithiomalonamides to paraffin oil, which is a lubricant, significantly increases the wear resistance of machine parts [87, 88].

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#### ԴԻԹԻՈՄԱԼՈՆԴԻԱՄԻԴՆԵՐԸ ՈՐՊԵՍ ՈՒՆԻՎԵՐՍԱԼ ՌԵԱԳԵՆՏՆԵՐ ՀԵՏԵՐՈՑԻԿԼՆԵՐԻ ԵՎ ԿՈՈՐԴԻՆԱՑԻՈՆ ՄԻԱՑՈՒԹՅՈՒՆՆԵՐԻ ՍԻՆԹԵԶԻ ՀԱՄԱՐ

## Վ. Վ. ԴՈՑԵՆԿՈ, Ա. Ե. ՍԻՆՈՑԿՈ

Ակնարկային Հոդվածում ներկայացված են ընդՀանուր դրույԹներ դիԹիոմալոնդիամիդների ստացման վերաբերյալ, մասնավորապես` դիԹիոմալոնդիանիլիդների քիմիայի մասին: Սույն աշխատանքը Հիմնված է «Ակտիվ մեԹիլենԹիոամիդները և սելենոամիդները որպես ունիվերսալ շինանյուԹեր Հետերոցիկլիկ քիմիայում» ղեկույցի վրա, որը ներկայացված է եղել Երևանում «NewTrendsChem-2023» միջաղդային դիտաժողովին 2023 Թ. սեպտեմբերի 24-ից 28-ը:

## ДИТИОМАЛОНДИАМИДЫ КАК УНИВЕРСАЛЬНЫЕ РЕАГЕНТЫ ДЛЯ СИНТЕЗА ГЕТЕРОЦИКЛОВ И КООРДИНАЦИОННЫХ СОЕДИНЕНИЙ

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В обзоре представлены данные об общих методах синтеза дитиомалондиамидов с акцентом на химию дитиомалондианилида. Данная работа основана на докладе конференции «Активные метилентиоамиды и селеноамиды как универсальные строительные блоки в гетероциклической химии», представленном на конференции «Новые тенденции в химии» (NewTrendsChem-2023) (24-28 сентября 2023 г., Ереван, Армения).

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