SYNTHESIS OF TETRA(1,4-DITHIACYCLOHEXENE)PORPHYRAZINE AND ITS METAL COMPLEXES

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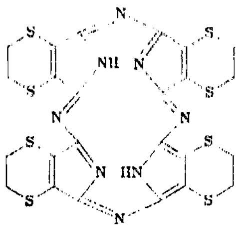
The syntheses of tetra(1,4-dithiacyclohexene)porphyrazine and its lithium salt, obtained by reaction of 3,6-dithiahexene-1,2-dicarbonitrile with lithium amylate, are described. A series of metal complexes of tetra(1,4-dithiacyclohexene)porphyrazine has been synthesized starting from 3,6-dithiacyclohexene-1,2-dicarbonitrile and the salts of the corresponding metals as well as from the free ligand and metal chlorides.

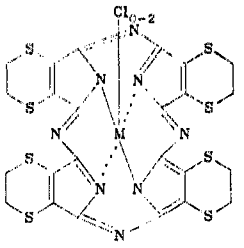
Compounds including the tetraazaporphine ring have found wide application in the most varied fields of science and technology, being used as dyes, organic semiconductors, catalysts, etc. [1-3].

The preparation of tetraazaporphines in which the pyrrole rings are condensed with heterocycles is of definite interest. Literature data on compounds of this type are limited [4-6] and an investigation of them would be of great interes in studying the effect of heterosubstitution on physical chemical properties as well as because of the possibility of their practical utilization.

In this paper, the syntheses of tetra(1,4-dithiacyclohexene)porphyrazine, H_2TDTP (I), and its metal complexes, Cl_{0-2}MTDTP (II-XVII) are described.



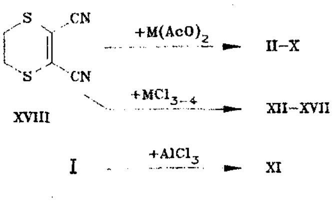
H_2TDTP (I)



Cl_{0-2}MTDTP (II—XVII)

II $M=Cu^{2+}$, III $M=Zn^{2+}$, IV $M=Mg^{2+}$, V $M=Cd^{2+}$, VI $M=F^{2+}$, VII $M=Co^{2+}$, VIII $M=Ni^{2+}$, IX $M=Pb^{2+}$, X $M=Sn^{2+}$, XI $M=Al^{3+}$, XII $M=Ga^{3+}$, XIII $M=In^{3+}$, XIV $M=Cr^{3+}$, XV $M=Ge^{4+}$, XVI $M=Sn^{4+}$, XVII $M=Zr^{4+}$

The syntheses of metal complexes II-XVII were carried out starting with 3,6-dithiacyclohexene-1,2-dicarbonitrile (SVIII) and salts of the corresponding metals (acetates or chlorides) in a melt or in boiling quinoline, (1) and (2), as well as by the reaction of the free ligand with the metal chlorides (3)



(1)

(2)

(3)

The central metal atoms in complexes with tri- and tetravalent metals have additional chlorine ligands.

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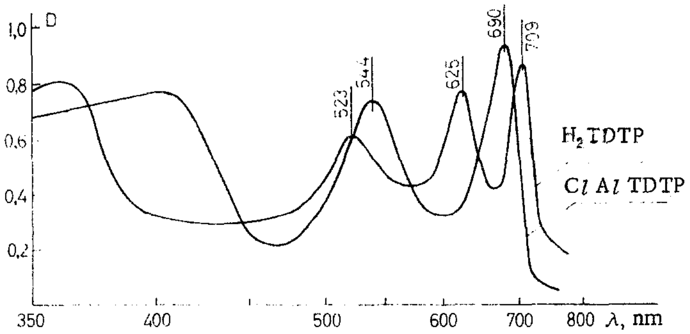

Fig. 1. Electronic spectra in α-chloronaphthalene.

In carrying out the reaction in a melt, we heated the mixture of starting materials to 180°C, after which the reaction mixture was observed to solidify and the temperature rose spontaneously to 220°C.

We monitored the completion of complex formation in reaction (3) by comparing the electronic spectra of I and the reaction mixture. We ended the synthesis when the absorption band at 625 nm, characteristic of starting compound I (Fig. 1), disappeared from the spectrum of the reaction mixture in α-chloronapthalene.

In order to prepare H_2TDTP (I), we synthesized its lithium complex (XIX) by reacting dinitrile XVIII with lithium amylate in boiling amyl alcohol:

$$\text{XVIII} \xrightarrow{C_5H_{11}OLi/C_5H_{11}OH} \text{XIX} \xrightarrow{H_2SO_4} \text{I}$$

When compound XIX is reprecipitated from concentrated sulfuric acid, it is completely demetallated to form compound I.

We prepared the starting dinitrile, XVIII, by reacting the disodium salt of dimercaptomaleindinitrile with dichloroethane in DMFA [1].

Compound I and its metal complexes were purified by washing with water and acetone in a Soxhelet apparatus and then subliming out volatile impurities in vacuum (10^{-3} Pa) at 200-230°C. For the stable metal complexes, II, VI-VIII, we also used reprecipitation from concentrated sulfuric acid. This method could not be used successfully to purify complexes III-V because they undergo demetallation. In the process of dissolution and subsequent reprecipitation from concentrated sulfuric acid, the complexes of tri- and tetravalent metals (XI-XVII) are found to change into the corresponding hydroxy derivative:

$$\text{XI-XVIII} \xrightarrow{H_2O/H_2SO_4} (OH)_2\text{MTDTP}$$

The individuality of the compounds synthesized was confirmed by elementary analysis and electronic spectroscopy.

H_2TDTP (I) and its metal complexes, II-XVII, appear as deeply colored, polycrystalline substances that do not melt on heating up to 500°C and do not sublime in vacuum. They are difficultly soluble in organic solvents.

EXPERIMENTAL

The electronic spectra of the compounds synthesized were taken in α-chloronaphthalene on a Specord UV-vis spectrophotometer at room temperature over a wavelength range of 330-760 nm. The starting 3,6-dithiacyclohexene-1,2-dicarbonitrile was prepared according to [1].

Tetra(1,4-dithiacyclohexene)porphyrazine H_2TDTP (I). Add 6.72 g (4 mmoles) of dinitrile XVIII to a mixture of 1.88 g (20 mmoles) of lithium amylate and 150 ml of amyl alcohol, heat to boiling (138-140°C), and stir for 6 h. Cool the reaction mixture to room temperature and dilute it with benzene to a 1:1 ratio. Filter off the precipitated solid, wash with benzene, and dry at 100°C. Then dissolve it in 200 ml of 18 M H_2SO_4 and pour the solution onto 400 g of crushed ice. Filter off the precipitated flocs, wash with water until the washings are neutral, and then with acetone in a Soxhelet apparatus. Dry at 100°C to obtain I in a 3.85 g yield (57%). Found: C 43.2, H 2.8, N 16.5, S 38.2%. Calculated for $C_{24}H_{16}N_8S_8$: C 42.8, H 2.5, N 16.7, S 38.0%.

TABLE 1. Yields and Elementary Analyses of Metal Complexes of Tetra(1,4-dithiacyclohexene)porphyazine, II-XVII

Compound	Found						Empirical formula	Calculated, %						Yield, %
	C, %	H, %	Cl, %	N, %	S, %	M		C, %	H, %	Cl, %	N, %	S, %	M	
II	39,1	2,4		15,0	34,7	8,8	$C_{24}H_{16}CuN_8S_8$	39,2	2,2		15,2	34,8	8,7	62
III	39,4	2,0		15,4	34,3	8,9	$C_{24}H_{16}N_8S_8Zn$	39,1	2,2		15,2	34,7	8,8	60
IV	41,6	2,5		16,0	36,5	3,3	$C_{24}H_{16}MgN_8S_8$	41,4	2,3		16,1	36,8	3,4	70
V	36,5	2,3		14,1	32,5	14,5	$C_{24}H_{16}CdN_8S_8$	36,7	2,0		14,3	32,7	14,3	65
VI	39,1	2,4		15,8	34,9	7,9	$C_{24}H_{16}FeN_8S_8$	39,6	2,2		15,4	35,2	7,7	54
VII	39,6	2,1		15,4	34,8	8,2	$C_{24}H_{16}CoN_8S_8$	39,4	2,2		15,3	35,0	8,1	63
VIII	39,5	2,2		15,1	35,1	8,0	$C_{24}H_{16}N_8NiS_8$	39,4	2,2		15,3	35,0	8,1	68
IX	32,9	1,9		12,4	29,0	23,8	$C_{24}H_{16}N_8PbS_8$	32,8	1,8		12,7	29,1	23,6	45
X	36,7	1,9		14,1	32,1	15,2	$C_{24}H_{16}N_8S_8Sn$	36,4	2,0		14,2	32,4	15,0	75
XI	39,4	2,1	4,6	15,3	34,7	3,9	$C_{24}H_{16}AlClN_8S_8$	39,2	2,2	4,8	15,2	34,9	3,7	83
XII	37,4	2,1	4,3	14,2	32,7	9,3	$C_{24}H_{16}ClGaN_8S_8$	37,1	2,1	4,5	14,4	32,9	9,0	53
XIII	35,2	2,0	4,2	13,0	31,4	14,1	$C_{24}H_{16}ClInN_8S_8$	35,0	1,9	4,3	13,6	31,1	14,0	61
XIV	37,9	2,3	4,5	14,6	33,4	7,2	$C_{24}H_{16}ClCrN_8S_8$	37,9	2,1	4,6	14,8	33,7	6,9	65
XV	35,1	2,2	8,5	13,6	31,3	9,2	$C_{24}H_{16}Cl_2GeN_8S_8$	35,3	2,0	8,6	13,7	31,4	9,0	45
XVI	33,2	1,8	8,0	13,2	29,9	13,9	$C_{24}H_{16}Cl_2N_8S_8Sn$	33,4	1,9	8,1	13,0	29,7	13,8	48
XVII	34,7	1,7	8,3	13,7	30,5	11,1	$C_{24}H_{16}Cl_2N_8S_8Zr$	34,5	1,9	8,5	13,4	30,7	10,9	74

Chlorotetra(1,4-dithiacyclohexene)porphyrazinealuminum ClAlTDTP (XI). Add a mixture of 6.74 g (1 mmole) of I and 13.5 g (500 mmoles) of aluminum chloride to 150 ml of quinoline and boil and vigorously stir for 8 h (235°C). Filter the hot reaction mixture and wash the precipitate on the filter with 200 ml of ethanol and then with water until chloride ion is absent from the filtrate. Purify further by extracting impurities with 200 ml of ethanol and 200 ml of acetone for 12 h in turn in a Soxhelet apparatus. Dry at 100°C to obtain complex XI.

Metal Complexes of Tetra(1,4-dithiacyclohexene)poryphyrazine (II-X). Heat a finely ground mixture of 10 mmoles of dinitrile XVIII and 5 mmoles of the appropriate metal acetate to 220°C and keep it for 30-40 min. Cool the reaction mixture to room temperature, powder it and purify it by extraction with water and acetone for 12 h in turn in a Soxhelet apparatus. Dry at 100°C. Complexes II and VI-VIII are further purified by reprecipitation from 18 M H_2SO_4.

XII-XIV. Mix a finely ground mixture of 5 mmoles of dinitrile XVIII and 22 mmoles of the appropriate metal chloride with 50 ml of quinoline, heat it to boiling (235°C) and hold it with stirring for 6 h. Cool the reaction mixture and dilute it with acetone to a 1:1 ratio. Filter off the precipitate, wash it with water until chloride ion is absent from the filtrate, then with 200 ml of acetone in a Soxhelet apparatus for 12 h. Dry at 100°C.

XV-XVII. Heat 20 mmoles of dinitrile XVIII (135°C) and add 10 mmoles of the appropriate metal chloride with stirring. Raise the temperature to 180°C, after which the reaction mixture spontaneously heats up to 220°C and solidifies. Cool the mass and powder it. In the case of complexes XV and XVI, wash the product with 300 ml of 0.5 M HCl and then with water until chloride ion is absent from the filtrate. Extract organic impurities by extraction in a Soxhelet apparatus for 10 h with 200 ml of benzene and 200 ml of acetone in turn. In the case of complex SVII, wash the product after the reaction mixture had cooled with acetone for 12 h in a Soxhelet apparatus.

All of the metal complexes synthesized, II-XVII, are held in vacuum (10^{-3} Pa) at 200-230°C for 2-4 h. The yields and elementary analyses are shown in Table 1.

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