[CONTRIBUTION FROM MONSANTO RESEARCH CORPORATION]

Coordination Compounds of Tris(2-hydroxyphenyl)-*s*-triazine and Derivatives[1]

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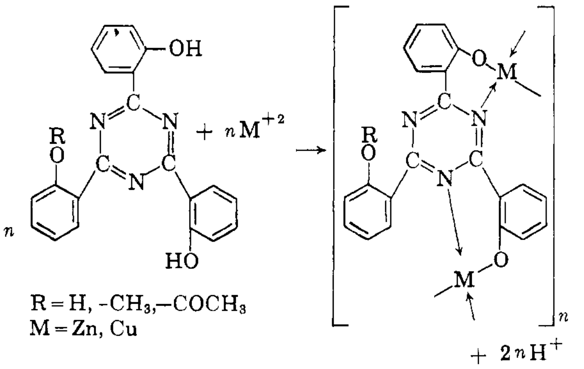
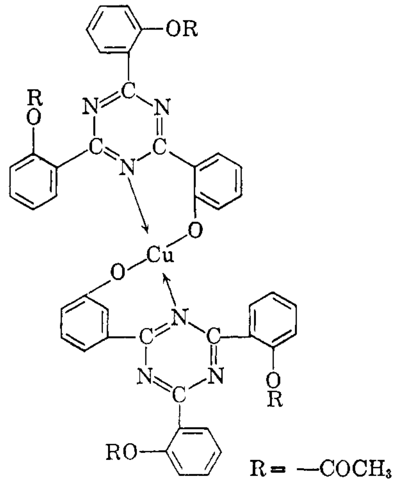
Tris(2-hydroxyphenyl)-*sym*-triazine is a coordinating ligand with three active sites for coordination with divalent tetracoordinate metal ions. Chelates with zinc, beryllium, manganese, iron, cobalt, nickel, copper, and magnesium have been made. The metal content of the chelates of the parent triazine and of its derivatives confirms the structures assigned. The zinc and beryllium chelates can be heated to 500° for one hour without measurable change in infrared spectra.

The structure of tris(2-hydroxyphenyl)-s-triazine indicates that it should be a powerful coordinating ligand and that it should hold metal ions at three sites. The rigidity of the structure forbids coordination of one metal ion by two sites in the same molecule. Thus, the products should be polymeric. Investigation of the zinc and beryllium compounds showed them to possess surprising thermal stability —withstanding a temperature of 500° for long periods without change. The infrared spectra before and after heating were identical.

Preliminary experiments showed that only two sites are active when the zinc and copper compounds are precipitated from solution. The beryllium compound, prepared without solvent, contains metal ions at all three sites. To clarify the structures of these compounds the mono-, di-, and triacetyl derivatives and the monomethoxyl derivative of the parent compound were prepared and their coordination compounds were studied. The monoacetyl and monomethoxyl derivatives gave coordination compounds with copper having the same ratio of copper to triazine as does the parent, unsubstituted compound. The composition indicates that they as well as the parent compound form linear coordination polymers.



The triacetyl derivative yielded no coordination compound when treated with copper acetate, as is to be expected. The diacetyl derivative coordinates readily with copper but the product contains one copper atom per two triazine molecules and accordingly is the simple compound.



The parent compound coordinates with beryllium at all three active sites when heated with anhydrous beryllium chloride in the absence of solvent and hence gives a crosslinked polymer. Such products could not be obtained from solution with zinc or copper acetates even when excess metal ion was employed. The extreme thermal stability of the zinc and beryllium coordination polymers compared with ordinary plastics makes them materials of great interest in the search for highly stable polymers.

EXPERIMENTAL

Salicylonitrile. Salicylaldoxime was refluxed with acetic anhydride for 2.5 hr. to give acetylsalicylonitrile,[2] which was then hydrolyzed with warm 10% potassium hydroxide solution. Acidification, extraction with ether, and recrystallization from benzene yielded salicylonitrile as a white crystalline solid, m.p. 99–100°, in 75% yield.

Tris(2-hydroxyphenyl)-s-triazine, I. The trimerization of salicylonitrile was accomplished in 100% yield by compressing a 30% solution of the nitrile in benzene to 6400 atm. at 160°. The reaction required 8 min. Recrystallization from nitrobenzene and from dioxane gave a yellow solid melting at 306–307°. Sublimation at 215–220°/10^{-4} mm. raised the melting point to 307–309°.

Anal. Calcd. for $C_{21}H_{15}N_3O_3$: C, 70.59; H, 4.23; N, 11.76. Found: C, 70.78; H, 4.28; N, 11.79.

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(2) V. Meyer and Bone, *Ber.*, **26**, 1254 (1893).

TABLE I

COORDINATION COMPOUNDS OF TRIS(2-HYDROXYPHENYL)-s-TRIAZINE AND DERIVATIVES

Metal	Ligand	Color	Method	Analysis		Ratio Liquid Metal
				Calcd.	Found	
Zn II	I	Yellow	A	15.54	14.95	1:1
Zn II	I	Yellow	B	21.63	20.75	1:1.5
Cu II	I	Green	A	15.17	15.30	1:1
Be II	I	Yellow	B	2.47	2.2	1:1
Be II	I	Yellow	C	3.67	3.5	1:1.5
Cu II	II	No reaction	A	—	—	—
Cu II	III	Green	A	13.79	13.32	1:1
Cu II	IV	Light green	A	6.75	6.79	1:1
Cu II	V	Green	A	14.68	14.53	1:1
Ni II	I	Yellow	A	14.18	12.69	1:1
Ni II	I	Yellow	B	14.18	16.29	1:1
Mn II	I	Dark brown	A	13.38	11.20	1:1
Fe II	I	Black	B	13.58	9.67	—
Co II	I	Orange	A	14.23	13.28	1:1
Mg II	I	Yellow	B	6.41	5.54	1:1

The compound was also prepared by heating salicylamide one hour at 260–270° as described by Cousin and Volmar.[3] After recrystallization from *N*,*N*-dimethylformamide a 35% yield of the triazine, m. p. 307–309°, was obtained.

Tris(2-acetoxyphenyl)-s-triazine, II. Efforts to prepare this compound by the high pressure condensation of acetylsalicylonitrile failed. When the pure liquid nitrile was heated to 150° at 6170 atm., no reaction occurred. At 6400 atm. and 250° a partial conversion to a dark brown solid took place. The solid did not melt at 325° and analysis did not agree with the expected composition.

Acetylation of 5 g. of I with 6 ml. of acetic anhydride in 30 ml. of pyridine was successful. After standing overnight at room temperature the solution was poured into a mixture of dilute hydrochloric acid and cracked ice. A white solid was obtained which was extracted with chloroform. The chloroform solution was washed successively with dilute acid, dilute alkali, and water. After drying over anhydrous sodium sulfate and evaporation of the solvent the product was recrystallized from benzene-ethanol mixture. Yield was 30%, m.p. 147–148°.

Anal. Calcd. for $C_{27}H_{21}N_3O_6$: C, 67.07; H, 4.38; N, 8.69. Found: C, 67.32; H, 4.64; N, 8.76.

2-(2-Acetoxyphenyl)-4,6-bis(2-hydroxyphenyl)-s-triazine, III. Partial acetylation was accomplished by treating 10.7 g. of I with 5.4 g. of acetic anhydride in 55 ml. of pyridine at room temperature for 66 hr. After processing the solution in the manner described above, the chloroform solution was concentrated to a small volume and diluted with petroleum ether. The resulting gummy solid was washed with petroleum ether and dried—wt. 9.9 g. Fractional crystallization from acetonitrile yielded two fractions. The minor fraction, 1.2 g. yellow solid, proved to be the monoacetyl derivative, m.p. 202°.

Anal. Calcd. for $C_{23}H_{17}N_3O_4$: C, 69.18; H, 4.29; N, 10.52. Found: C, 69.35; H, 4.30; N, 10.73.

2(2-Hydroxyphenyl)-4,6-bis(2-acetoxyphenyl)-s-triazine, IV. The second fraction from the above crystallization was a pale yellow solid. After two recrystallizations from benzene-ligroin 6.45 g. was obtained, m.p. 131–133°.

Anal. Calcd. for $C_{25}H_{19}N_3O_5$: C, 68.02; H, 4.34, N, 9.52. Found: C, 68.04; H, 4.53; N, 9.71.

2-(2-Methoxyphenyl)-4,6-bis(2-hydroxyphenyl)-s-triazine, V. To a cold (5°) solution of 10 g. of I and 20 g. of sodium hydroxide in 200 ml. of water and 100 ml. of methanol, 20 ml. of dimethyl sulfate was added with stirring. The precipitate was filtered and washed with water. Recrystallization from methyl ethyl ketone gave 3.4 g. (30% yield) of the yellow monomethoxyl derivative, m.p. 166–167°.

Anal. Calcd. for $C_{22}H_{17}N_3O_3$: C, 71.15; H, 4.62; N, 11.32; —OCH_3, 8.35. Found: C, 71.2; H, 4.5; N, 11.3; —OCH_3, 8.0.

Coordination Compounds. Three methods were used to prepare the chelates. These are illustrated by the following detailed procedures for zinc and beryllium chelates.

Method A. Preparation of zinc chelate. To the tris(2-hydroxyphenyl)-s-triazine (0.2 g., 0.6 mmole) dissolved in a minimum amount of dimethylformamide was added 0.176 g. (0.8 mmole) of zinc acetate dihydrate in dimethylformamide. A precipitate formed almost instantaneously. The reaction mixture was digested for 15 min. at about 60°. The filtered solid was then heated in boiling ethanol. A yellow solid, infusible to 360°, was obtained in quantitative yield.

Anal. Calcd. for $C_{21}H_{13}N_3O_3Zn$: Zn, 15.54. Found: Zn, 14.95.

Method B. Preparation of zinc chelate. The tris(2-hydroxyphenyl)-s-triazine (2.0 g., 6 mmoles), zinc acetylacetonate (2.4 g., 9 mmoles), and 20 ml. of *N*,*N*-dimethylformamide were refluxed for 40 min. (The solvent was added to prevent sublimation of the zinc acetylacetonate.) When the pot temperature reached 180°, a vacuum was gradually applied. The dry solid was heated at 200–220° for 10 min. The solid was washed with boiling benzene, then with acetone several times, and dried. The weight of the yellow powder was 2.3 g. It was infusible at 360°.

Anal. Calcd. for $C_{21}H_{12}N_3O_3Zn_{1.5}$: Zn, 21.63. Found: Zn, 20.75.

Preparation of beryllium chelate. The 2,4,6-tris(2-hydroxyphenyl)-s-triazine (1.072 g., 3 mmoles) and beryllium acetylacetonate (1.25 g., 6 mmoles) in 10 ml. of *N*,*N*-dimethylformamide was refluxed for 3 hr. The solution was heated by oil bath to 200–220° and then heated for 15 min. under high vacuum. The solid was treated with hot benzene and washed several times with acetone. The yellow solid was infusible at 360°. The yield was virtually quantitative.

Anal. Calcd. for $C_{21}H_{13}N_3O_3Be$: Be, 2.47. Found: Be, 2.20.

Method C. Preparation of beryllium chelate. The 2,4,6-tris(2-hydroxyphenyl)-s-triazine (10.7 g., 0.03 mole) and anhydrous beryllium chloride (5.0 g., 0.06 mole) were intimately mixed in a 50-ml., round-bottomed flask fitted with air condenser and nitrogen inlet. The dry mixture was heated to 315–330° (both temperature) for 6 hr. under nitrogen. The reaction mixture was boiled in *N*,*N*-dimethylformamide to remove the ligand, filtered, washed with acetone, and air dried. The yellow solid was boiled in alcohol to remove any

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[3] Cousin and Volmar, *Bull. soc. chim. France* (4) 15, 416(1914).

remaining beryllium chloride and again dried. The bright yellow solid was infusible at 360°.

Anal. Calcd. for $C_{21}H_{12}N_3O_3Be_{1.5}$: Be, 3.67. Found: Be, 3.5.

The Mn and Co ions have coordinated with the ligand in approximately the 1:1 ratio; however, the true valency of the metal ions is in doubt. They may be trivalent, carrying a hydroxyl or other small ion. It is obvious that the metal content of the linear polymer has the ligand metal ratio 1:1 only when the chain length is infinite. In the actual cases shown in Table I the metal content depends on the chain length and the nature of the terminal groups. For short chains of five to twenty ligand units the metal content will be too low if the terminal groups are ligand molecules and will be too high if the chains end with metal ions. The conditions required for production of long chain polymers are being investigated.

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Synthesis of Some Thiol Esters of *dl-cis-trans*-Chrysanthemummonocarboxylic Acid

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A number of new thiol esters of *dl-cis-trans*-chrysanthemummonocarboxylic acid have been synthesized. The 1,4-piperazonium dichrysanthemummonocarboxylate and chrysanthemummonocarboxypiperidide were also made.

Some of the esters of *dl-cis-trans*-chrysanthemummonocarboxylic acid (*dl-cis-trans*-2,2-dimethyl 3-isobutenylcyclopropane-1-carboxylic acid) possess potent insecticidal properties.[1–4] However, thiol esters of chrysanthemummonocarboxylic acid have not been described in the literature.

The present paper deals with the synthesis of the following thiol esters: methyl, ethyl, propyl, isopropyl, *n*-butyl, allyl, furfuryl, piperonyl, and 6-bromopiperonyl.

The thiol esters were made by a modification of the procedure described by Harper and Reed[5] for the preparation of ethyl *dl-trans*-carbomethoxythiocaronate. The yields of the thiochrysanthemummonocarboxylates were uniformly good except for the piperonyl and 6-bromopiperonyl compounds, which were unstable to heat, and troublesome to prepare, purify, and analyze. The infrared spectra of the thiol esters in chloroform solution exhibited the characteristic band for the carbonyl frequency of a thiol ester in the region of 1675 cm.^{-1} [6]

Piperonal, dissolved in absolute ethanol, yielded on treatment with dry ammonia and hydrogen sulfide gas dipiperonyldisulfide sulfhydrate as the principal product. This is contrary to the findings of Manchot and Zahn,[7] who obtained mainly the disulfide under similar conditions and the sulfhydrate under more drastic experimental conditions. The reduction of this compound to the piperonyl mercaptan proceeded smoothly with lithium aluminum hydride, using the general procedure of Arnold *et al.*[8] for reducing disulfides to mercaptans. 6-Bromopiperonal subjected to the same reaction as piperonal yielded a mixture of 6,6′-dibromodipiperonyl disulfide and 6,6′-dibromodipiperonyl disulfide sulfhydrate. These two compounds were separated by fractional crystallization. On subsequent reduction with lithium aluminum hydride, both yielded 6-bromopiperonyl mercaptan which, unlike the piperonyl mercaptan, proved to be unstable to heat, since it lost bromine and sulfur on attempted purification by distillation with steam. These three bromine intermediates have not been previously described.

1,4-Piperazonium dichrysanthemummonocarboxylate and chrysanthemummonocarboxypiperidide were also made. The former is a well defined crystalline solid which can be used as a derivative for the characterization of chrysanthemummonocarboxylic acid. The piperidide is a liquid possessing possible synergistic properties in insecticides.

The results of the insecticidal testing of the present compounds will be reported separately.

EXPERIMENTAL[9]

Alkyl thiochrysanthemummonocarboxylates. In a typical preparation (*n*-butyl thiol ester), a solution of 0.027 mole of freshly distilled *dl-cis-trans*-chrysanthemummonocarbonyl chloride in 7 ml. of dry benzene was added dropwise during the course of 1 hr. to a mechanically stirred solution of 0.032 mole of the mercaptan in 7 ml. of dry benzene to which 2.6

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