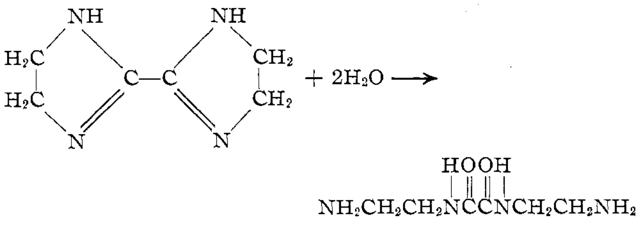
compound.[12] Admittedly the infrared evidence is not at all definitive in these regions of the spectrum, but the nature of the bonding site on the ligand can at least be held open for the moment. It is interesting that the closely related ligand, 2,2′-biimidazole, also exhibits anomalous chelating ability.[13]

Hydrolysis of 2,2′-Bi-2-imidazoline.—The ligand hydrolyzed in aqueous solution according to the following equation to give N,N′-bis(2-aminoethyl)oxamide.



$$NH_2CH_2CH_2\overset{H}{N}\overset{O}{C}\overset{O}{C}\overset{H}{N}CH_2CH_2NH_2$$

The hydrolysis product appears to be dibasic with $pK_{a_1} = 8.30$ and $pK_{a_2} = 9.54$ at 25° in a 1.0 *M* KNO_3 solution. A rapid titration of the original ligand gave approximate constants pK_{a_1} and pK_{a_2} of 3.8 and 7.7, respectively.

All of the metal ion complexes appeared to hydrolyze, the original complexes not being recoverable after dissolution in water. Apparently the rate of hydrolysis was quite slow, judging from the 15,600 cm.$^{-1}$ band in the Cu(II) complex spectrum which shifted gradually to about 16,000 cm.$^{-1}$ over a 2-day period. During this time the solution changed from blue-green to pale violet in color. Although insufficient quantities of complex were isolated for elemental analysis, an infrared spectrum of the blue solid obtained after hydrolysis shows that the compound is likely a complex of N,N′-bis(2-aminoethyl)oxamide.

Woodburn and O'Gee[14] reported that 2,2′-bi-2-imidazoline was soluble in water to give a basic solution and yielded ethylenediamine and oxalic acid after refluxing several hours with 10% NaOH. The rapid hydrolysis of biimidazoline in hot water to ethylenediamine and oxalic acid was reported by Reggel, Henry, and Wender.[15] No intermediate species were reported. It was found in the present work that the ligand hydrolyzed in either hot (100°) or cold water, but the hydrolysis product was N,N′-bis(2-aminoethyl)oxamide. No ethylenediamine or oxalate ion was detected unless a more drastic condition was used, such as refluxing with 10% NaOH. The composition and characteristics of the possible metal ion complexes of this intermediate as well as the further hydrolysis to ethylenediamine complexes await further studies.

Acknowledgments.—The authors wish to thank Dianne Waltner and Gerald Goe for doing the preliminary work on these compounds, Clarence Hildebrand for synthesizing the material, and the Public Health Service (Research Grant GM 10353) for partial financial support.

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CONTRIBUTION FROM THE INSTITUTE OF INORGANIC CHEMISTRY,
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Concerning the Synthesis of Dithio-α-diketone Complexes of Transition Metals from Thiophosphates of 1,2-Dithiols

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Received June 25, 1965

The synthesis of transition metal complexes of dithio-α-diketones of composition $M(S_2C_2R_2)_n$ (n = 2, 3) from metal salts, acyloins, and P_4S_{10} is described. The reaction of benzoin with P_4S_{10} is shown to produce a mixture of isomeric thiophosphates of stilbenedithiol. Evidence is presented for the latter as the main organic solvolysis product. Small amounts of the acid $(C_6H_5)_2C_2S_2PS_2H$ are formed during the partial hydrolysis of the thioester mixture. The stable nickel chelate $((C_6H_5)_2C_2S_2PS_2)_2Ni$ is described. The reaction of the thioesters with $Fe(CO)_5$ affords the complex $(C_6H_5)_2C_2S_2Fe_2(CO)_6$.

Introduction

Recently,[3,4] a general method of preparation of transition metal complexes of dithio-α-diketones $M(S_2C_2R_2)_n$ (n = 2 or 3) has been developed which utilizes the easily accessible acyloins and P_4S_{10} for the synthesis of the novel bidentate sulfur-containing ligands. In the present paper details of this reaction are reported.

General Description of the Method

In the preferred procedure the acyloin is first heated with a 3- to 6-fold molar excess of P_4S_{10} in an inert organic solvent (*e.g.*, xylene or dioxane). The thiolation of the acyloin is exothermic and accompanied by the evolution of H_2S; most of the P_4S_{10} dissolves during

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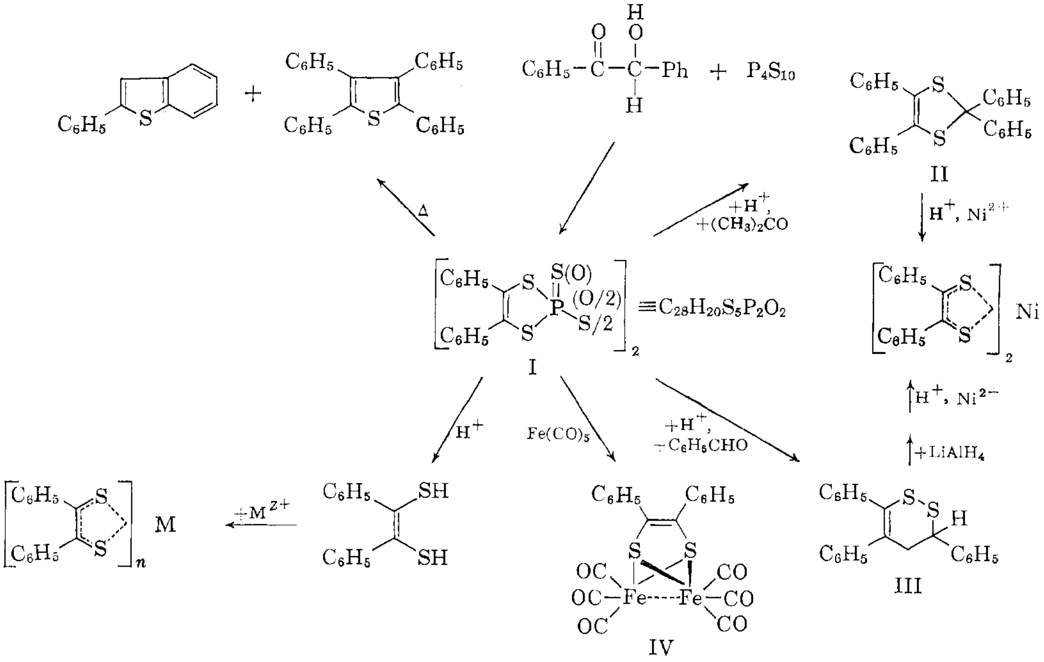
[3] G. N. Schrauzer, V. P. Mayweg, H. W. Finck, U. Müller-Westerhoff, and W. Heinrich, *Angew. Chem.*, **76**, 345 (1964); *Angew. Chem. Intern. Ed. Engl.*, **3**, 381 (1964); G. N. Schrauzer, H. W. Finck, and V. P. Mayweg, *Angew. Chem.*, **76**, 715 (1964); *Angew. Chem. Intern. Ed., Engl.*, **3**, 639 (1964).

[4] G. N. Schrauzer and V. P. Mayweg, *J. Am. Chem. Soc.*, **87**, 1483 (1965).

this reaction but most of the excess recrystallizes upon cooling. The resulting solutions contain thioesters of the corresponding dithiols and are stable on storage. To prepare the metal complexes, solutions of the metal salts (*e.g.*, acetates, halides, acetylacetonates, etc.) in water or alcohol are added and the mixtures are heated. The presence of a solvolyzing agent is essential; when anhydrous metal salts are employed the reaction usually does not go to completion. Owing to the reducing properties of the thioester solution the anions of the complexes are formed first; salts of the anions $M(S_2C_2R_2)_n^{-z}$ (z = 1, 2) may be isolated by adding quaternary ammonium, phosphonium, or arsonium salts. The metal salts are preferably employed in low valence states; otherwise a larger excess of the thioester solution must be used since part of the dithiol is oxidized to sulfur-containing by-products (with R = phenyl, 2,3,5,6-tetraphenyldithiadiene is formed) which are sometimes difficult to separate from the complexes. Purification of the complexes may be achieved either by reduction to the anion with hydrazine and subsequent oxidation through reacidification or preferably by column chromatography on silica using benzene as eluent. Among the acyloins the diaryl derivatives react particularly cleanly, while alkyl acyloins form the active thioesters in lower yield, producing volatile malodorous by-products. Where available, α-haloketones may be employed in place of the acyloins. The thiophosphate of 1,2-phenylethylenedithiol, for instance, is more conveniently prepared by allowing α-bromoacetophenone to react with P_4S_{10} than by way of benzoyl carbinol or phenylglyoxal. Attempts to prepare the unsubstituted complex by this route were so far unsuccessful. However, the recent isolation[5] of the disodium salt of ethylenedithiol makes this ligand accessible as well, and a number of the basic unsubstituted complexes $M(S_2C_2H_2)_n$ have already been prepared.[6-8] The CN-substituted complexes are likewise obtained *via* the sodium salt.[9]



The Constitution of the Thioesters

Although it was stated previously that thiophosphoric esters of the dithioacyloins are formed in the reaction of acyloins with P_4S_{10},[3,4] no such compounds have yet been reported. For the model experiments to be described in the following, benzoin was selected for reasons mentioned above. The evaporation of the thioester solution afforded an amber resin, for which the analysis corresponds most nearly to $C_{28}H_{20}S_5P_2O_2$; it is clearly soluble in benzene and other organic solvents and hydrolyzes in neutral, alkaline, or acidic solution. The final solvolysis products in acidic solution are phosphoric acid, H_2S, and stilbenedithiol, a compound which is known to undergo self-condensation to tetraphenyldithiadiene and polymeric dithiobenzil.[10] It may be trapped as a cyclic ketal (II) by acid solvolyzing the thioester in the presence of acetone. If benzaldehyde is used instead, a compound with the probable structure III is isolated. Iron pentacarbonyl also reacts, producing the red complex IV.[11,12] These and several other reactions are shown schematically. The infrared spectrum of I shows a P=O stretch at 1214 cm.$^{-1}$; bands at 1050 and 943 cm.$^{-1}$ indicate P—O and P—O—P bonds. Although partly covered by the phenyl absorptions, a band at 752 cm.$^{-1}$ suggests the

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(5) W. Schroth and J. Peschel, *Chimia*, **18**, 171 (1964).

(6) G. N. Schrauzer and V. P. Mayweg, *J. Am. Chem. Soc.*, **87**, 3585 (1965).

(7) E. Hoyer and W. Schroth, *Chem. Ind.*, (London), 652 (1965).

(8) G. N. Schrauzer, V. P. Mayweg, and W. Heinrich, *ibid.*, 1464 (1965).

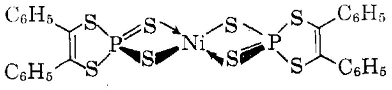
(9) G. Bähr and G. Schleitzer, *Chem. Ber.*, **90**, 438 (1957).

(10) G. N. Schrauzer and H. W. Finck, *Angew. Chem.*, **76**, 143 (1964); *Angew. Chem. Intern. Ed. Engl.*, **3**, 133 (1964); R. Mayer and M. Nitzschke, *Chem. Ber.*, **96**, 2359 (1963).

(11) More convenient methods of preparation of complexes of this type have been developed (G. N. Schrauzer and W. Heinrich, to be published); also see R. B. King, *J. Am. Chem. Soc.*, **85**, 1584 (1963), for preparation of the CF_3-substituted compound.

(12) The X-ray structural analysis, confirming structure IV, has been completed: personal communication, R. Bryan.

presence of P=S bonds. The P—S stretching vibrations appear as a broad band with a maximum at 518 cm.$^{-1}$ and shoulders at about 490, 455, and 440 cm.$^{-1}$, respectively. Evidently, the ester solution is a mixture of various thioesters of the general structure I. A separation into the individual components was not attempted in view of the high viscosity of the products. Pertinent additional information has been obtained, however, from the partial hydrolysis of the thioester solution in the presence of Ni^{2+} ions. If a small amount of water is employed and a reaction temperature of 40° is maintained, the major product is still $NiS_4C_4(C_6H_5)_4$; however, from the filtrate a yellow-brown complex of composition $C_{28}H_{20}S_8P_2Ni$ crystallized, which must have structure V.



V

Its isolation provides evidence for the intermediate occurrence of minor amounts of the acid $(C_6H_5)_2C_2S_2PS_2H$ during the hydrolysis of the ester mixture.

Experimental

Isolation of the Ester Mixture.—The preparation of the thiophosphoric ester solution of stilbenedithiol has already been described.[4] A solution made up from 100 g. of benzoin and 150 g. of P_4S_{10} in 700 ml. of xylene was allowed to stand for several days, during which time excess P_4S_{10} crystallized out of the solution. An aliquot was evaporated *in vacuo* at steam-bath temperature. A viscous, amber residue was obtained which solidified to a clear resin. *Anal.* Calcd. for $C_{28}H_{20}S_6P_2O_2$: C, 55.1; H, 3.3; S, 26.2; P, 10.1; mol. wt., 610. Found: C, 55.5; H, 4.0; S, 25.2; P, 7.3; mol. wt., 550. It is readily soluble in benzene, xylene, dioxane, and other solvents, yielding clear solutions which produce complexes $M(S_2C_2R_2)_n$ when heated with metal salt solutions. The thermal decomposition afforded a mixture of (mainly) 2-phenylthionaphthene with tetraphenylthiophene (both compounds were identified by comparison of the infrared spectra).

Preparation of the Cyclic Dimethylketal of Stilbenedithiol.—A thioester solution made from 50 g. of benzoin and 50 g. of P_4S_{10} in 400 ml. of dioxane was mixed with 1 l. of acetone and 150 ml. of concentrated HCl and refluxed for 3 hr. After cooling the solution was slowly added to 2 l. of dilute NaOH (1 *N*). Subsequent extraction with *n*-hexane and recrystallization from acetone–water afforded 7 g. of product, m.p. 112°. *Anal.* Calcd. for $C_{17}H_{16}S_2$: C, 71.9; H, 5.7; S, 22.5; mol. wt., 284.3. Found: C, 72.1; H, 5.7; S, 22.5, mol. wt., 282. The n.m.r. spectrum (in CCl_4 at 60 Mc.) shows two single peaks at 1.91 and 7.08 p.p.m. *vs.* TMS as the internal standard, with intensity ratio of 6:10. The ketal was heated in tetrahydrofuran solution with concentrated HCl in the presence of $NiCl_2$ for 5 hr. Dilution with H_2O and extraction with benzene gave a green organic phase from which $NiS_4C_4(C_6H_5)_4$ was isolated.

Preparation of $C_{21}H_{16}S_3$ (Compound III).—To 100 ml. of a thioester solution prepared as in the previous experiment, 90 ml. of freshly distilled benzaldehyde and 10 ml. of concentrated HCl were added. After refluxing for 5 hr., the solution was allowed to cool. The product (2.5 g.) crystallized out of this solution and was isolated. Recrystallization from xylene afforded slightly yellow needles, m.p. 232°. *Anal.* Calcd. for $C_{21}H_{16}S_3$: C, 69.2; H, 4.42; S, 26.4; mol. wt., 367. Found: C, 68.3; H, 4.5; S, 26.3; mol. wt., 367. The compound was reduced with $LiAlH_4$ in warm tetrahydrofuran. After hydrolysis and acidification, bis(dithiobenzil)nickel was obtained by adding a Ni^{2+} solution. The compound contains no -SH group, as evidenced by the infrared spectrum and by standard chemical tests.

Reaction of the Thioester Solution with $Fe(CO)_5$.—The xylene solution of the thioester was heated with an excess of $Fe(CO)_5$. Vigorous evolution of CO and the precipitation of a black material (FeS) occurred while the solution became deeply red. After filtration and evaporation of the solution the residue was dissolved in benzene and chromatographed on a column of silica. The complex was finally recrystallized from methanol; the wine-red needles decompose at 126°. *Anal.* Calcd. for $C_{20}H_{10}S_2Fe_2O_6$: C, 46.0; H, 1.9; S, 12.3; Fe, 21.4; mol. wt., 521.8. Found: C, 45.8; H, 2.2; S, 12.3; Fe, 20.9; mol. wt., 523.

Isolation of $Ni(S_2PS_2C_2(C_6H_5)_2)_2$ (VI).—To 500 ml. of a thioester solution from 100 g. of benzoin in dioxane, 100 ml. of a saturated solution of $NiCl_2$ in water was added, and the mixture was carefully warmed to 40°. After 20 min. the complex $NiS_4C_4(C_6H_5)_4$ (yield 50 g.) was filtered off and the filtrate was cooled. Yellow-brown crystals (8 g.) separated after several days of standing and were recrystallized from CH_2Cl_2 by Soxhlet extraction. The complex is diamagnetic and sparingly soluble in most solvents. *Anal.* Calcd. for $C_{28}H_{20}S_8P_2Ni$: C, 45.8; H, 2.7; S, 35.0; P, 8.4; Ni, 8.0. Found: C, 45.8; H, 2.8; S, 35.6; P, 8.4; Ni, 8.0. Upon heating VI decomposes at 265°, producing a mixture of 2-phenylthionaphthene and tetraphenylthiophene as the volatile organic products. Infrared spectrum: 3048 (s), 3030 (s), 1600 (m), 1582 (m), 1557 (s), 1488 (s), 1477 (s), 1256 (m), 1181 (s), 1162 (m), 1107 (w), 1076 (s), 1033 (s), 1002 (s), 980 (s), 911 (m), 855 (vs), 840 (vs), 820 (s), 752 (s), 742 (vs), 695 (vs), 647 (vs), 613 (vs), 595 (s), 571 (vs), 517 (s), 498 (m), 467 (m), 445 (w), 349 (s), 323 (s) cm.$^{-1}$ (in KBr). The band at 571 cm.$^{-1}$ is assigned to the P=S···Ni stretch; the bands at 517, 498, 467, and 445 cm.$^{-1}$ are the P—S and the bands at 349 and 323 cm.$^{-1}$ the Ni—S stretching vibrations.