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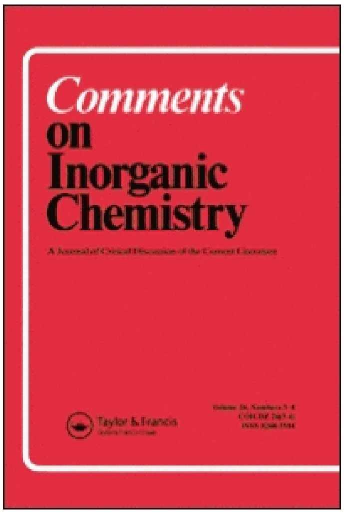

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Facts and Fantasy on Tetrathio Oxalate—Activation and Condensation of Carbon Disulfide

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Facts and Fantasy on Tetrathio Oxalate—Activation and Condensation of Carbon Disulfide

In its reactions with electron-rich metal centers, including the mercury cathode, CS_2 undergoes a wide variety of reactions to produce C_nS_m groups in varying charges and coordination modes. The coupling of two CS_2 molecules to formally give C_2S_4 group has been shown to produce three different moieties:

(a) Coupling via C–S bond formation to produce an $\overline{\mathrm{MC(:S)SC(:S)S}}$ ring.
(b) Coupling via C–C bond formation to formally produce ethenetetrathiol.
(c) Coupling via electroreductive dimerization to produce stable tetrathio oxalate salts.

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INTRODUCTION

It was only in 1977 that one of the pioneers of modern inorganic carbon disulfide chemistry, G. Gattow, wrote in his monograph on carbon sulfides and their inorganic and complex chemistry "in contrast to the opinion of earlier investigators the existence of tetrathio oxalate, tetrathio oxalic acid, and its esters cannot be considered as proven."[1] Indeed, despite several claims for the synthesis of tetrathio oxalate and intensive efforts during recent years for the head-to-head reductive dimerization of CS_2 it was not until the early eighties that tetrathio oxalate was isolated and crystallographically characterized.

The first to accomplish the reductive dimerization of a carbon dichalcogenide was Kolbe, who in 1868 passed CO_2 over molten sodium[2]:

$$2\,\mathrm{Na_l} \xrightarrow[360\ ^\circ\mathrm{C}]{2\,\mathrm{CO_2}} \mathrm{Na_2C_2O_4}.$$

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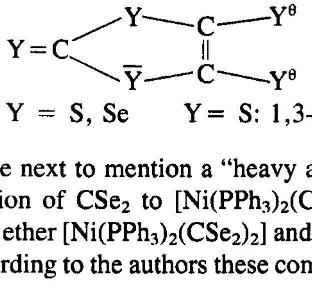
The first to claim that he had obtained tetrathio oxalate was Fetkenheuer,[3] who reduced carbon disulfide with sodium amalgam in ammonia medium. There is even a patent in 1973 which claims the preparation of tetrathio oxalate.[4] The early reduction was repeated in numerous laboratories using different reductants and media (electrochemically,[5] sodium amalgam, sodium in liquid ammonia or in HMPT, potassium in DMF or sodium naphthalenide in DMF). In all cases it turned out that instead of $Me_2C_2S_4$, the dimethylthioether of a multisulfur dithiolate system, $Me_2C_3S_5$ was isolated with an elemental composition very close to $Me_2C_2S_4$. Dimethyltrithiocarbonate was formed as a byproduct.[5,6] A further treatment of the reduction mixture was done in most cases to obtain the methylation products as the desired derivatives:

$$4\ CS_2 + 4e^- \xrightarrow{\text{methylation}} Me_2C_3S_5 + Me_2CS_3.$$

Similarly, carbon diselenide has been reduced electrochemically, yielding the corresponding selenium heterocycle.[7] With carbon sulfide-selenide the mixed sulfur–selenium compound is formed which obviously is a diselenolate according to a preliminary x-ray diffraction study[8]:



Y = S, Se   Y= S: 1,3-dithiole-2-thione-4,5-dithiolate

The next to mention a "heavy atom" oxalate was K. A. Jensen[9]: By addition of CSe_2 to $[Ni(PPh_3)_2(CO)_2]$ or $[Rh(PPh_3)_3Cl]$ in anhydrous ethyl ether $[Ni(PPh_3)_2(CSe_2)_2]$ and $[Rh(PPh_3)_2(CSe_2)_2Cl]$ were obtained. According to the authors these compounds probably contain coordinated tetraseleno oxalate ion formed by "oxidative addition" of two molecules f carbon diselenide to Ni(O) or to Rh(I), respectively. Though reasonable, no further proof of the identity of these $(CSe_2)_2$ species was provided.

The first to prepare dimethyl tetrathio oxalate was Hartke and his group at Marburg.[10] They started with 4,5-bis(methylthio)-1,3-dithiole-2-thione and via 4,5-bis(methylthio)-1,3-dithiole-2-thione from photochemical decarbonylation isolated the crystallized ester as a very reactive monomer which behaves like a dithiabutadiene system. Dimethyl tetrathio oxalate either reacts with dienes as a [2π] component (only one thiocarbonyl group) or with olefins and acetylenes as a [4π] component to form [2 + 4] cycloadducts.[11] So far attempts to dealkylate the dithioester have failed.

It has since been shown by HPLC that the tetrathio oxalate dianion is one among at least six intermediates present in the electrolytic reduction of CS_2 in dimethylformamide.[12] It emerges from the same study that trithio carbonate is formed after the electrochemical reduction of CS_2 in the standing mixture.

The first to hold crude yellowish grey potassium tetrathio oxalate in his hands, prepared electrochemically from CS_2 in acetonitrile, was the present author when he was with Henning Lund at Aarhus in 1981.[13]

The first to report the electrosynthesis of bis-tetraethylammonium tetrathio oxalate was P. Jeroschewski.[14]

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TRANSITION METAL PROMOTED HEAD-TO-TAIL COUPLING OF CARBON DISULFIDE

Besides the desired head-to-head $S_2C–CS_2$ dimerization of CS_2 there is a different activation of carbon disulfide by electron rich rhodium complexes, which display a tendency to condense sulfur-containing ligands. Both *trans*-$[RhCl(CO)(DPM)]_2$ (DPM = $Ph_2PCH_2PPh_2$) and $[Rh_2Cl_2(\mu\text{-}CO)(DPM)_2]$ react with CS_2 to form $[Rh_2Cl_2(CO) + (C_2S_4)(DPM)_2]$ as the final product of each reaction.[15] X-ray crystallography reveals that the C_2S_4 fragment contains two intact CS_2 molecules fused at C(4)–S(3) (using the numbering scheme of Figure 1, axial DPM ligands not depicted). This fragment is then bound to one rhodium atom Rh(1) via S(1) and C(5), and to the other rhodium atom Rh(2) through S(4). The

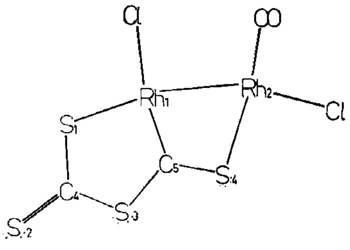

FIGURE 1 Coupling of CS_2 via C–S bond formation.

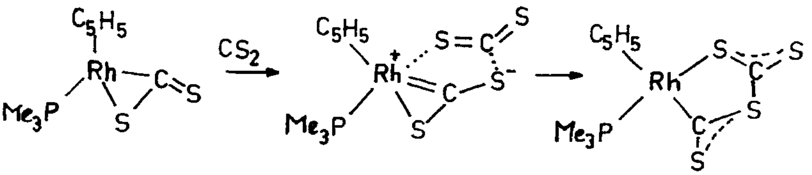

FIGURE 2 Coupling of dihapto-coordinated CS_2 on CS_2.

red complex crystallizes with two independent molecules per asymmetric unit. Both dimers have the same overall geometry, with the Rh centers bridged by two transoid DPM ligands, but differ slightly in the orientations of the ligands. Within the resulting RhC_2S_4 metallocycles the C–S distances and angles compare with those reported for [Rh(h^5-C_5H_5)(C_2S_4)(PMe_3)],[16] where an analogous five-membered RhSCSC metallo heterocycle was observed.

The head-to-tail C_2S_4 ligand can be considered a carbene ligand $C_2S_4^{2-}$, with each of the coordinated sulfur atoms and the carbene atom functioning as two-electron donors to the rhodium atoms. Therefore, the rhodium atoms are formally Rh(II). The postulated reaction sequence includes a stepwise addition of two CS_2 molecules: A metal-carbon-bound CS_2 intermediate (RH– –(S:)C(:S)– –Rh) is electrophilically attacked at one of the sulfur atoms by another CS_2 molecule resulting in head-to-tail condensation. The formation of the monomeric compound [Rh(h^5-C_5H_5)(C_2S_4)(PMe_3)] is interpreted as a 1,3-dipolar addition of the Rh–C–S moiety of the dihapto-bound CS_2 product at one thiocarbonyl group of CS_2 (Figure 2).

TRANSITION-METAL-PROMOTED HEAD-TO-HEAD COUPLING OF CARBON DISULFIDE

Orange $Fe_4(CO)_{12}(C_2S_4)$ was isolated in 1%–2% yield as one of five products from the reaction of $Fe_3(CO)_{12}$ with an excess of CS_2 in hexane at 80 °C under pressure (CO–Ar 1:1, ~10 atm, 2–18 h).[17] In this complex two centrosymmetrically related $Fe_2(CO)_6$ units are each attached by both iron atoms to each of two thiolate groups of a C_2S_4 ligand via a 1,1- and 2,2-dithio chelating ring linkage. The molecular parameters [C–C bond length of 133(1) pm and C–S bond length of

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177 pm (average)] are viewed in terms of the C_2S_4 ligand being formally a derivative of ethenetetrathiol rather than a tetrathio oxalate ligand.

Reaction of $Ni_2(h^5\text{-}C_5H_5)_2(\mu\text{-}CO)_2$ with CS_2 at 40 °C for several hours produces a black-green solution, from which $[Ni_3(h^5\text{-}C_5H_5)_3(\mu_2\text{-}S)]_2(C_2S_4)$ was obtained as the major product and isolated by chromatography over alumina with toluene solvent.[18] Similarly, $Ni_2(h^5\text{-}C_5Me_5)_2(C_2S_4)$ was isolated as the sole product from the analogous reaction with $Ni_2(h^5\text{-}C_5Me_5)_2(\mu_2\text{-}CO)_2$. According to x-ray structural determinations the hexanickel as well as the dinickel molecules represent metal bis(1,2-dithiolenelike) C_2S_4 complexes formed by a head-to-head $S_2C\text{–}CS_2$ dimerization of carbon disulfide through activation on the transition metal centers. The 1,2-dithiolenelike chelation of each of the two $Ni(h^5\text{-}C_5Me_5)$ moieties in the dinickel complex by the tetradentate C_2S_4 ligand results in the formation of a planar $NiS_2C_2S_2Ni$ core. The diamagnetic dinickel tetrathiolenelike complex has crystallographic C_{2h} – $2/m$ site symmetry. The $NiS_2C_2S_2Ni$ core of this bimetallic tetrathiolene complex experimentally possesses a planar geometry with extensive π-electron delocalization indicated from its bond lengths and redox properties. The Ni–S, S–C and C–C bond lengths of 212.2(1), 171.8(3) and 136.0(11) pm, respectively, are similar to those found in the neutral nickel bis(1,2-dithiolene) complexes. The quantitative dimerization of CS_2 is attributed to each Ni(I) in the coreactant functioning as a one-electron reductant as well as a chelating sulfur acceptor (Figure 3). The highly delocalized π-electron system with reversible redox character was established by cyclic voltammetry (Table I). In contrast to the results found for the bimetallic tetrathiolenelike complex, the π system of the bimetallic-coordinated 1,2-dithio oxalate ligand is only weakly delocalized.[19] According to the authors the hexanuclear nickel complex may be considered an adduct of the above dinuclear complex formed by the net insertion of a $(h^5\text{-}C_5H_5)Ni\text{–}S\text{–}Ni(h^5\text{-}C_5H_5)$ fragment across each pair of nickel-

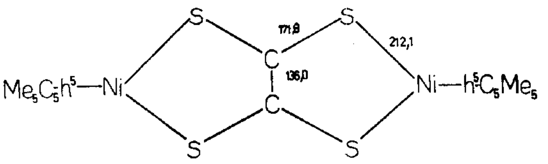

FIGURE 3 Bond lengths in $Ni_2(h^5-C_5Me_5)_2(C_2S_4)$ with planar NiC_2S_4 core (pm).

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TABLE I

$E_{1/2}$ values for $Ni_2(h^5\text{-}C_5Me_5)_2(C_2S_4)$(S.C.E., CH_2Cl_2, 0.1 M TBAH)

Couple	$[Ni_2]^-/[Ni_2]^{2-}$	$[Ni_2]^0/[Ni_2]^-$	$[Ni_2]^+/[Ni_2]^0$
$E_{1/2}$ (V)	−1.43	−0.92	+0.09

chelated sulfur atoms to give two equivalent, six-membered, chairlike $(NiS)_3$ rings.

ELECTROREDUCTION OF CARBON DISULFIDE: SYNTHESIS, STRUCTURE AND COMPLEX CHEMISTRY OF TETRATHIO OXALATE

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Electrochemical reduction of carbon disulfide at a mercury pool cathode at 0 °C in acetonitrile saturated with potassium iodide at −1.0 V (vs Ag/AgCl) gives a brownish potassium tetrathio oxalate that dissolves in water, forming a red solution from which the tetraphenylphosphonium salt is precipitated with Ph_4PCl.[13] Recrystallization from acetonitrile-diethylether yields orange crystals analyzed as $(Ph_4P)_2C_2S_4 \cdot 2\ H_2O$. Recrystallization from water produces orange needles containing 6 mol of water of crystallization. The crystals were large enough for an x-ray examination. Their structure consists of an I-centered arrangement of the PPh_4^+ ions in a cell with the *c* axis halved. The anions and water molecules are placed in holes in this lattice. The tetrathio oxalate ion is placed across a twofold axis but is far from planar, the torsion angle being 79.5°(1.0), in contrast to the oxalates which are usually planar or nearly so, but analogous to the torsion angle in potassium dithio oxalate (76.5°). The large torsion angle prevents close contact between the sulfur atoms but may also be enforced by the lattice. Indeed, four water molecules in the similar hole *c*/2*c* away are arranged in almost the same way as the four sulfur atoms. The most important dimensions are given in Table II. The C–C bond (146 pm) is apparently shorter than the bond in oxalate (156–158 pm); the C–C length in potassium dithio oxalate is 151.6 pm.

The potentiostatic reduction of CS_2 in acetonitrile with tetraethylam-

TABLE II
Selected distances and angles of bis(tetraphenylphosphonium)-tetrathio oxalate hexahydrate

Distance	pm	Angle	Degrees
C–S1	171.3(9)	S1–C–S2	128.6(6)
C–S2	169.1(10)	S1–C–C′	114.7(8)
C–C′[a]	146.1(19)	S2–C–C′	116.6(8)
S2–S2′	306.8	Torsion angle	
S1–S2′	353.0	S1–C–C′–S2′	79.5(1.0)

[a] The mark ′ denotes symmetry relation $2 - x$, $1 - y,z$.

monium bromide as supporting electrolyte is sensitive to the carbon disulfide concentration. At values greater than 1.5 M a hexathio peroxydicarbonate is formed as the bis(tetraethylammonium)salt[14] (besides trithio carbonate and 1,3-dithiole-2-thione-4,5-dithiolate). Under proper conditions (CS_2 = 0.5 M) the current yield in $C_2S_4^{2-}$ is as high as 75%.

How is tetrathio oxalate formed? Carbon disulfide is a weaker electron acceptor and a better donor than carbon dioxide. The twofold degenerate $1\pi_g$ HOMO of CS_2 is essentially sulfur centered. Therefore, metal ions can attack at thiocarbonyl sulfur. On the other hand the $(2\pi_u)$ LUMO is more heavily concentrated on carbon. It is energetically higher than the corresponding orbital of CO_2. Thus the electron affinity of CS_2 is lower. Nevertheless if an additional electron is accepted it is concentrated on carbon, leading to the V-shaped radical anion. In this radical anion the degeneracy of the $2\pi_u$ orbital is lifted. The new HOMO has only 50% carbon character and is 25% sulfur concentrated. This means that nucleophiles can be added carbophilically as well as thiophilically which partly explains the different metal activation of CS_2 by electron-rich metal centers. Degeneracy lifting also explains the new bands and red shift in the electronic spectrum of the radical anion compared with CS_2.[20]

There are now also strong arguments from pulse-radiolytic experiments[21] that the primary reduction product of CS_2 is the radical anion $CS_2{\cdot}^-$: In aqueous solution containing *t*-butanol (4.3M)e_{aq}^- reacts with CS_2 with a rate constant of 3.3×10^9 dm^3 mol^{-1} s^{-1} to form $CS_2{\cdot}^-$. The relatively stable carbon disulfide radical anion has an optical absorption spectrum with λ = 275 nm ($\varepsilon = 2 \times 10^4$ dm^3 mol^{-1} cm^{-1}) and λ = 350 nm

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($\varepsilon = 5 \times 10^3$ dm^3 mol^{-1} cm^{-1}). It decays by reaction with oxygen. Protonation according to

$$CS_2^{\cdot -} + H_3O^+ \rightarrow CS_2H\cdot + H_2O$$

yields $CS_2H\cdot$ which absorbs at 320 nm ($\varepsilon = 6 \times 10^3$ dm^3 mol^{-1} cm^{-1}).

Obviously it is the same radical anion $CS_2^{\cdot -}$ that is formed during electrolysis and dimerizes to tetrathio oxalate, provided that no further reactions can take place. Exclusion of water and oxygen is therefore essential. The procedure for isolation of tetrathio oxalate then is as tricky as it is simple: Take a supporting electrolyte, the cation of which forms a slightly soluble salt with the tetrathio oxalate dianion (see above).

If $C_2S_4^{2-}$ is not scavenged it can react further with excess carbon disulfide present in the reaction mixture. What follows from a NDDO total energy calculation[22] is that

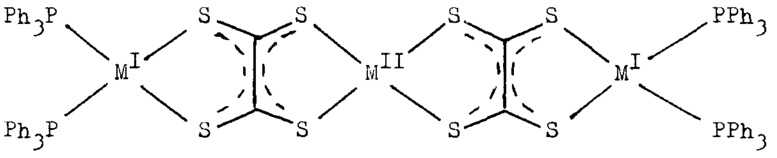
$$C_2S_4^{2-} + CS_2 \xrightarrow{+2e} C_3S_5^{2-} + S^{2-}$$

is an uphill process (solvent stabilization not taken into account), but

$$S^{2-} + CS_2 \rightarrow CS_3^{2-}$$

is energetically highly favored, thus overcompensating the overall energy need.

$C_2S_4^{2-}$ forms at least three types of complexes: dinuclear, homo- and heterometallic trinuclear and polynuclear. With heavy metal cations tetrathio oxalate forms deeply colored 1:1 compounds which precipitate from aqueous solution and are obviously polynuclear complexes with bridging C_2S_4 groups. The wet precipitates dissolve with solutions of chlorotris(triphenylphosphine)metal(I) complexes in dichloromethane to deep blue solutions from which, after concentration and addition of a proper solvent, trinuclear complexes of type (a) crystallize (tris-complexes are formed with trivalent central ions).



(a)

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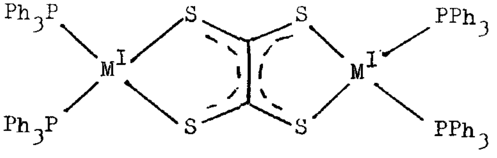
Direct combination of tetrathio oxalate (as water/pyridine solution of an alkali salt of the ligand) and a pyridine solution of a "phosphine lidded" metal halide yields intensely colored binuclear C_2S_4-bridged complexes [type (b)] which can be precipitated as microcrystals by addition of water.



(b)

Thus tetrathio oxalate opens easy pathways to a great variety of di- and trinuclear complexes with extensive electron delocalization.

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