

Studies on Binary Carbon Sulfides and Their Metal Complexes

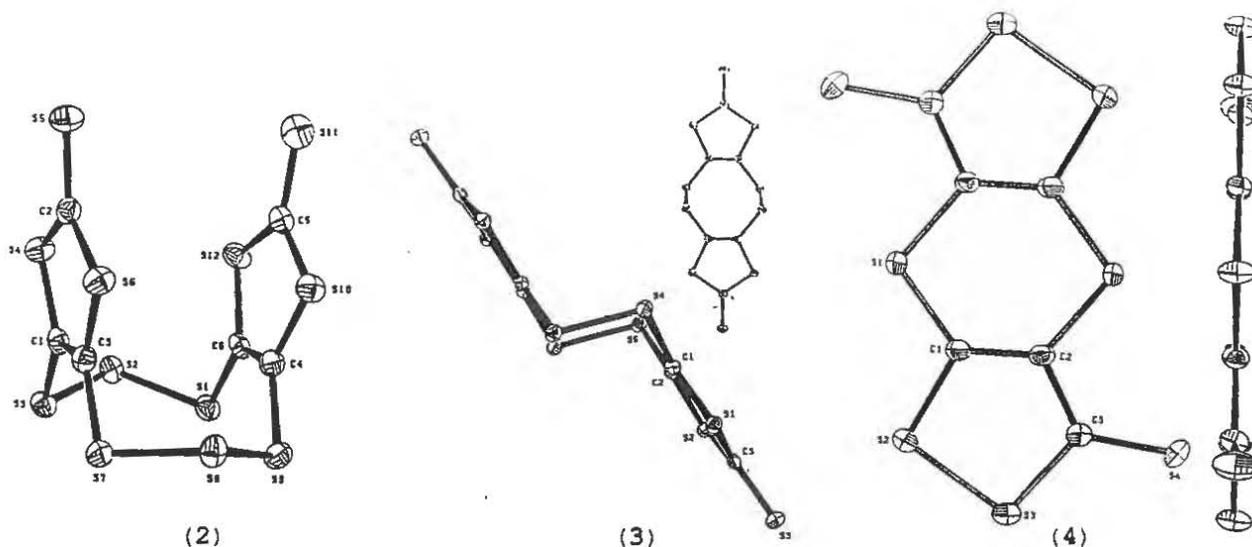
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Our research on carbon sulfides was motivated by an interest in new materials which might have useful chemical and physical properties [1]. Previous work has demonstrated that structurally and electronically novel materials can be obtained with simple stoichiometries such as $(\text{CH})_x$, $(\text{CN})_x$, $(\text{BN})_x$, and $(\text{SN})_x$ [2].

Seven stable molecular carbon sulfides were known before we started our work [1,3,4]. We found that the reaction of $\text{Cp}_2\text{TiC}_3\text{S}_5$ with one equivalent of S_2Cl_2 gave two new carbon sulfides C_3S_8 (1) and C_6S_{12} (2) [3]. The eclipsed conformation of the C_3S_5 rings in C_6S_{12} (2) is noteworthy.

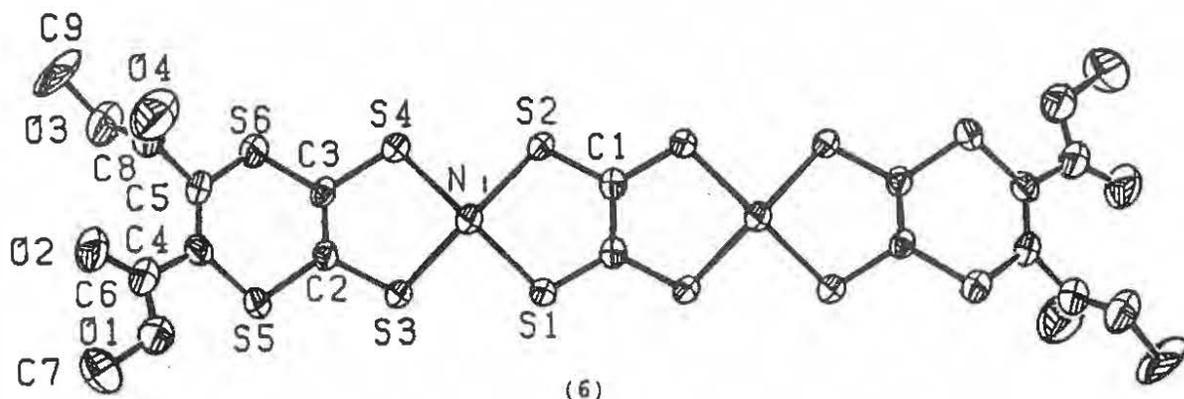


The inorganic "tetrathiocin" $\alpha\text{-C}_6\text{S}_{10}$ (3) was prepared from the oxidation of $[\text{Zn}(\alpha\text{-C}_3\text{S}_5)_2]^{2-}$ with SO_2Cl_2 . This synthesis is accompanied by the formation of what we believe to be polymeric $(\text{C}_3\text{S}_5)_n$. The crystal structure of (3) revealed that C_6S_{10} molecules stack in the crystal to form a 2-dimensional layered structure with CS_2 solvate in the channels formed by these layers [5]. (3) was found to react with dimethylacetylenedicarboxylate (DMAD) to give $\text{C}_3\text{S}_5\cdot\text{DMAD}$. This can be hydrolyzed to give $\text{OC}_3\text{S}_4\cdot\text{DMAD}$, a precursor to new tetrathiafulvalenes and new dithiolenes.

In $[\text{Zn}(\beta\text{-C}_3\text{S}_5)_2]^{2-}$ the $\text{C}_3\text{S}_5^{2-}$ ligand features adjacent ring sulfur atoms. The reaction of $[\text{Zn}(\beta\text{-C}_3\text{S}_5)_2]^{2-}$ with SOCl_2 gave $\beta\text{-C}_6\text{S}_8$ (4) and $\beta\text{-C}_6\text{S}_{10}$ (5). $\beta\text{-C}_6\text{S}_8$ (4), the first known planar 1,4-dithiin, features fused 1,2-dithiole-3-thione rings conjugated with a central 1,4-dithiin ring to form a 22 π electron system. The reactions of DMAD with 1,2-dithiole-3-thione functional group in $\beta\text{-C}_6\text{S}_{10}$ affords several new organosulfur heterocycles.

Studies on the coordination chemistry of $\text{C}_2\text{S}_4\cdot\text{DMAD}^{2-}$ uncovered the first planar C_2S_4 complex (6). Crystal structure analysis confirmed the planarity of the 15Å long $\text{Ni}_2\text{C}_6\text{S}_{12}$ core in $\{\text{C}_2\text{S}_4[\text{Ni}(\text{C}_2\text{S}_4\cdot\text{DMAD})_2]_2\}^{2-}$. The

cyclic voltammogram of (6) exhibits four redox couples corresponding to 4-/3-, 3-/2-, 2-/1-, and 1-/0.



The hydrolysis of the bicyclic $C_2S_4(CO)_2$ followed by the addition of S_2Cl_2 and $(dppe)NiCl_2$ gave $(dppe)Ni(C_4S_{11})$ (7). The structure of the $C_4S_{11}^{2-}$ chelate is thought to resemble a subunit in $(C_2S_4)_x$. Attempts to prepare C_2S_x from $[(MeCp)_2Ti]_2(\mu-C_2S_4)$ afforded hydrocarbon-contaminated samples of the desired polymer. We found that this Ti_2 compound reacts with S_8 to give the dinuclear compound $[(MeCp)_2Ti]_2(\mu-C_2S_4)(\mu, \eta^2-S_2)$ (8).

The reaction of $C_2S_4(CO)_2$ and MS_4^{2-} ($M = Mo, W$) gives $[M(S_2C_2S_2CO)_3]^{2-}$, COS, and sulfur [6]. Similarly, $C_2S_4(CO)(CS)$ and WS_4^{2-} gives $[W(S_2C_2S_2CS)_3]^{2-}$. Electrochemical studies show that $[M(S_2C_2S_2CE)_2]^{2-}$ ($M = Mo, W; E = S, O$) undergo two one-electron oxidations at mild potentials giving the charge neutral inorganic complexes MC_6S_{15} and $MC_6O_3S_{12}$.

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