NCS^-, contains an N-bonded thiocyanate and exhibits no tendency to rearrange to the S-bonded isomer in either the solid state or solutions.[32] Since all of the other factors are kept constant, the difference in the bonding in the chromium(0) and manganese(I) species must be attributed to the charge on the metal. Thus, the driving force for the stabilization of the S-bonded isomer of a more positive manganese(I) may be the latter's preference for the polarizable end of the thiocyanate, which enhances Mn=CO π-bonding in the complex. In $Cr(CO)_5NCS^-$ the extent of Cr=CO π-bonding, as evidenced by the positions of the CO stretching frequencies, is already considerable, and hence the metal may exhibit little tendency to bond to the more polarizable sulfur atom. Unfortunately, no data are available at present to check the validity of the above supposition.

In order to assess further the effect of the metal charge on the nature of M–CNS attachment, attempts were made to synthesize the iron derivative, $Fe(CO)_4(CNS)_2$. However, no thiocyanatocarbonyl complex could be isolated and characterized from three different reactions tried.

Studies on solutions of thiocyanatopentacarbonylmanganese(I) reveal that equilibria between the two linkage isomers are attained rapidly and are sensitive to the nature of the solvent employed. Perhaps the most striking example of solvent importance in stabilizing a given mode of manganese–thiocyanate attachment is the behavior of the complex in acetonitrile. Addition of CH_3CN promotes formation of the isothiocyanate whereas removal of the solvent affords the S-bonded complex. These and previously mentioned observations (*vide supra*) indicate that the energy difference between the two isomers is indeed very small.

It is of interest to note that the isomerization of some saturated organic thiocyanates proceeds more readily in acetonitrile than in less polar solvents such as benzene and methyl ethyl ketone.[33] Although close analogy between these and our results is not justified—the former is a kinetic and the latter a thermodynamic effect—it is possible that mechanistically the rearrangements in acetonitrile are similar, and most probably involve ionization followed by a recombination of the ions. The conductivity data on $Mn(CO)_5NCS$ solutions are consistent with the presence of ionic species; however, this does not preclude other mechanisms, for example, an intramolecular rearrangement.

Finally, a rather unusual feature in the spectrum of $Mn(CO)_5NCS$ in acetonitrile merits a brief comment. The A_1^1 stretching mode of the N-bonded isomer (Table I) also gives rise to an absorption at a considerably lower frequency (*ca.* 40 cm.$^{-1}$) than that of the halogenopentacarbonyl complexes.[31] Similar positions of this band in the spectra of the two linkage forms of $Mn(CO)_5CNS$ indicate that the Mn=CO(1) bond orders are comparable. No satisfactory explanation in terms of manganese–thiocyanate bonding is available for this phenomenon at present. Quantitative studies on the kinetics and mechanism of the isomerization and on the equilibria in solution, which are now in progress, may help to resolve the problem.

Acknowledgment.—The financial support of this investigation by the National Science Foundation is gratefully acknowledged.

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The Synthesis of 1-Thia-4-telluracyclohexane (1,4-Thiatellurane) and Four of Its Addition Compounds

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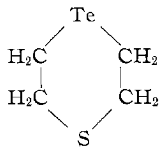
The previously unreported heterocyclic compound, 1-thia-4-telluracyclohexane, C_4H_8STe, has been synthesized by reaction of β,β′-dichlorodiethyl sulfide (mustard gas) with tellurium and sodium formaldehydesulfoxylate (rongalite) in aqueous solution. 1-Thia-4-telluracyclohexane is a white, crystalline solid (m.p. 69.5°) which forms crystalline addition compounds of the type $C_4H_8STeX_2$ with chlorine, bromine, and iodine, and a telluronium salt $[C_4H_8STeCH_3{}^+]I^-$ with methyl iodide.

An area of research under investigation in these laboratories involves synthetic, structural, and thermodynamic studies of the sulfur, selenium, and tellurium analogs of 1,4-dioxane.[1] The present paper describes the synthesis of 1,4-thiatellurane by reac-



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[1] J. D. McCullough, *Inorg. Chem.*, **3**, 1425 (1964), and references therein.

tion of β,β′-dichlorodiethyl sulfide (mustard gas) with a solution of tellurium in alkaline aqueous sodium formaldehydesulfoxylate (rongalite).[2] Although the yield (6.6%) is low, the procedure is simple and requires only 3–4 hr. for completion.

As expected by analogy with similar tellurium compounds, thiatellurane reacts to form crystalline addition compounds with the halogens and methyl iodide. The preparation and properties of four of these compounds are described.

Experimental

Ventilation.—Because of the toxic nature of mustard gas and the repulsive and persistent odor of thiatellurane, all synthetic work described here was (and should be) carried out in a well-ventilated fume hood.

Materials.—Unless otherwise stated below, reagents were of an analyzed grade and solvents were Eastman White Label products.

X-Ray Diffraction.—Small single crystals of 1,4-thiatellurane were sealed in thin-walled glass capillaries to prevent vaporization and oxidation of the specimens. Precession, rotation, and Weissenberg (zero and upper level) photographs about the *b* axis were prepared by use of Cu Kα (λ 1.542 Å.) radiation.

β,β′-Dichlorodiethyl Sulfide.—Mustard gas was prepared from technical grade thiodiglycol (Matheson Coleman and Bell) by the method of Reeves and Love.[3] The product was heated at 80–85° under a pressure of ~30 mm. for 1 hr. to remove water and HCl.

1,4-Thiatellurane.—Sodium formaldehydesulfoxylate (Eastman practical grade, 180 g. or 1.50 moles), tellurium powder (Matheson Coleman and Bell 99.5%, 40 g. or 0.31 g.-atom), and NaOH pellets (120 g. or 3.0 moles) were mixed in a 2-l., three-necked flask. Water (800 ml.) was added and the mixture brought to reflux for 15 min. under a current of nitrogen gas. An inert atmosphere was maintained in this manner throughout the synthesis and steam distillation in order to minimize oxidation of the thiatellurane. Mustard gas (48 g. or 0.30 mole) in 120 ml. 95% ethanol was then added slowly from a dropping funnel over a period of 30 min. while gentle reflux was maintained. The volatile, white thiatellurane collected in the cooler, upper portion of the flask during this period, while a large quantity of small spherical beads of an apparently insoluble white solid formed in the liquid.

The apparatus was then modified for steam distillation with a coolant-coil-type condenser and a receiver immersed in an ice-water mixture. The first distillate was largely ethanol but was later shown to contain some thiatellurane. When the temperature of the vapors rose to 90°, the receiver was changed and the distillation continued. Much of the thiatellurane collected on the condenser coils as a light yellow solid, but this was transferred to the receiver from time to time by interrupting the flow of cooling water through the condenser. Thus it was possible to note when thiatellurane ceased to distil. While still cold, the distillate was filtered and the crude product was found to weigh 4.1 g. Recrystallization from methanol gave a nearly white solid melting at 69.5°. A small but pure additional yield (0.2 g.) was obtained from the initial (ethanol) fraction by addition of ice water. The total yield was thus 4.3 g. or 6.6% based on mustard.

Anal. Calcd. for C_4H_8STe: C, 22.26; H, 3.74. Found: C, 22.27; H, 3.76.

Mixture Melting Points.—Melting points of intimate mixtures of recrystallized 1,4-thiatellurane with pure, 1,4-thiaselenane[4] (m.p. 107.0–107.5°) were observed as follows: 20 mole % thiaselenane, m.p. 70.0–71.2°; 50 mole % thiaselenane, m.p. 82–87°.

$C_4H_8STeI_2$.—A solution of iodine in ethylene chloride (22.1 ml. of 0.048 *M* I_2 or 0.00106 mole of I_2) was added to 0.229 g. (0.00106 mole) of thiatellurane in 10 ml. of ethylene chloride. Fine, garnet-red needles formed immediately and were filtered out (0.220 g.). An additional yield of larger well-formed orthorhombic prisms was obtained by evaporation of the filtrate. The total yield was 0.484 g. or 97%. The product was recrystallized from ethylene chloride, m.p. 150–151° dec.

Anal. Calcd. for $C_4H_8STeI_2$: C, 10.23; H, 1.72. Found: C, 10.32; H, 1.78.

$C_4H_8STeBr_2$.—A solution of Br_2 in carbon tetrachloride (0.875 *M*) was added dropwise to 0.203 g. (0.000940 mole) of thiatellurane in 10 ml. of ethylene chloride. A curdy, yellow-orange precipitate was formed locally but this was dissolved by shaking. The addition was continued until 1.06 ml. (0.00093 mole of Br_2) had been added. On standing, a light yellow, dense, crystalline solid formed. The recovered yield was 0.242 g. or 68%. This was recrystallized from ethylene chloride, m.p. 191–192° dec.

Anal. Calcd. for $C_4H_8STeBr_2$: C, 12.79; H, 2.15. Found: C, 12.98; H, 2.28.

$C_4H_8STeCl_2$.—A solution of Cl_2 in carbon tetrachloride (0.625 *M*) was added dropwise to 0.363 g. (0.00168 mole) of thiatellurane in 15 ml. of ethylene chloride. A curdy, white precipitate formed locally after each addition but was dissolved by shaking. A very small amount of insoluble, black material also formed and accumulated. After 2.60 ml. of Cl_2 solution (0.00162 mole of Cl_2) had been added, the mixture was warmed and filtered. On cooling, the filtrate yielded 0.19 g. (41%) of crude product. Recrystallization from ethylene chloride gave thin, white plates, m.p. 201–202° dec.

Anal. Calcd. for $C_4H_8STeCl_2$: C, 16.76; H, 2.81. Found: C, 16.86; H, 2.76.

$[C_4H_8STeCH_3]^+I^-$.—Methyl iodide (1.1 g., 0.0078 mole) was added to 0.132 g. (0.000610 mole) of thiatellurane in 5 ml. of acetone. A precipitate of fine, white plates formed almost immediately. The yield (0.18 g. or 82%) was recrystallized from 95% ethanol. The substance showed no sharp melting or decomposition temperature, but there was considerable darkening and some sublimation between 200 and 230°.

Anal. Calcd. for $C_5H_{11}STeI$: C, 16.79; H, 3.10. Found: C, 16.96; H, 3.13.

Results and Discussion

X-Ray Crystallography of 1,4-Thiatellurane.—The X-ray diffraction photographs of 1,4-thiatellurane indicate isomorphism with 1,4-thiaselenane, 1,4-dithiane, and 1,4-diselenane. Crystallographic data for the first two compounds are given in Table I and data on the other two are tabulated in ref. 4. All four compounds crystallize in the monoclinic space group $P2_1/n$ ($P2_1/c$) with two molecules in the unit cell, a situation which requires the molecules to be at least statistically centrosymmetric. In thiatellurane and thiaselenane this indicates a random disorder in which the unlike ends of the molecules are indistinguishable. For this

TABLE I

X-RAY CRYSTALLOGRAPHIC DATA FOR 1,4-THIATELLURANE AND 1,4-THIASELENANE

	1,4-Thiatellurane	1,4-Thiaselenane
a, Å.	7.018 ± 0.010	6.867 ± 0.006
b, Å.	5.730 ± 0.015	5.552 ± 0.010
c, Å.	8.274 ± 0.010	7.956 ± 0.006
β, deg.	92.70 ± 0.10	93.13 ± 0.10
Density, g. cm.$^{-3}$		
X-Ray	2.155	1.832
Flotation	2.10	1.81

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(2) M. L. Bird and F. Challenger, *J. Chem. Soc.*, 570 (1942).

(3) A. M. Reeves and S. Love, *Science*, **107**, 204 (1948). Note precautions therein regarding the handling of mustard gas.

(4) J. D. McCullough and P. Radlick, *Inorg. Chem.*, **3**, 924 (1964).

reason, a complete structural study of 1,4-thiatellurane was not attempted; however, a study of the structure of a least one of the halogen addition compounds is planned.

Further evidence of isomorphism of thiatellurane and thiaselenane is found in the melting points of mixtures. These observations suggest continuous miscibility in the solid state.

Formation of Polymer.—In the first synthesis of 1,4-thiatellurane only 400 ml. of water was used and the mustard was not diluted with ethanol. The yield of thiatellurane in that case was 0.76 g. or only 1.2%. Along with this, 22 g. of a nonvolatile, insoluble material was recovered. This was presumed to be a linear polymer of the type $[-S-(CH_2)_2-Te-(CH_2)_2-]_n$ formed in competition with the cyclic monomer. The structure and properties of the polymer are under investigation.

Hydrolytic Loss of Mustard.—The yields of polymer and thiatellurane account for about 35% of the mustard. The remaining mustard was presumably lost through competitive reaction of the cyclic sulfonium ion intermediate with water.[4,5] Two variations in procedure were tried in an attempt to reduce the hydrolytic loss of mustard. In the first of these the water was replaced by 400 ml. of ethanol. The reaction of tellurium with rongalite was slow and incomplete and no thiatellurane was found in the distillate. In the second case, the reaction between tellurium and rongalite was carried out in 100 ml. of water, the mixture cooled, 300 ml. of ethanol added, and again refluxed while the mustard (dissolved in 100 ml. of ethanol) was added. About 0.2 g. of polymer was formed but no thiatellurane was isolated.

Although it might be possible to improve the per cent yield of thiatellurane by following the procedure used for 1,4-thiaselenane,[4] this would involve the synthetic sequence

$$Te \longrightarrow Al_2Te_3 \longrightarrow H_2Te \longrightarrow Na_2Te$$

followed by reaction of sodium telluride with mustard in absolute ethanol. This would be an unpleasant and time-consuming process and product isolation would be more difficult. For these reasons, further efforts to improve the yield of thiatellurane were confined to the simpler rongalite procedure.

Effect of Dilution on Yield of Monomer.—On the assumption that the production of the cyclic monomer would be favored over the polymer by increasing the volume of the system the effect of dilution was studied. An increase in the volume of water from 400 to 800 ml. increased the yield of thiatellurane to 2.0%. A still greater increase (to 6.6%) resulted when 800 ml. of water was used and the 38 ml. of mustard was diluted with 120 ml. of ethanol. It is probable that the per cent yield of 1,4-thiatellurane could be increased still further by going to higher dilutions. However, this would require the use of larger reaction flasks and equipment or starting with smaller quantities of the reactants. The former would make the synthesis more unwieldy, while the latter would reduce the actual yield. Increasing the volume of ethanol to 200 ml. (or more) might be beneficial but this would also increase losses in the solvent. Thus, it is believed that the described conditions are near optimum for a small-scale synthesis.

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(5) P. D. Bartlett and C. G. Swain, *J. Am. Chem. Soc.*, **71**, 1406 (1949).

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The Interaction of Dibenzenechromium with Lewis Acids

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Dibenzenechromium reacts with symmetrical trinitrobenzene, p-quinone, chloranil, and tetracyanoethylene in benzene solution to form deeply colored compounds containing one molecule of dibenzenechromium to one molecule of the Lewis acid. The ultraviolet, infrared, and electron spin resonance spectra of these compounds are discussed and suggest that the complexes are best described as dibenzenechromium salts of radical anions.

The structure of dibenzenechromium has recently received considerable attention with evidence being presented for delocalization[1] of the π-electron system in the benzene ring as well as for a localized system[2] in which each ring attains a Kekulé-like structure. Unlike ferrocene and its derivatives, bisarenechromium

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(1) F. A. Cotton, W. A. Dollase, and J. S. Wood, *J. Am. Chem. Soc.*, **85**, 1543 (1963).

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