



Models for disorder in thiourea host/guest adducts
by James Francis Fait

A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in
Chemistry

Montana State University

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Abstract:

Thiourea host/guest adducts display a variety of types of disorder of the guest molecules. As these adducts also exhibit dramatic selectivity in the guest molecules included in the adduct, models that accurately describe the disorder of the guest are required to assess the principle forces involved in the formation of these adducts. Crystallographic structural studies for eight adducts of thiourea have been completed and disorder models for each adduct have been developed. Thermodynamic data on two adducts was collected for assessing the magnitude of the interactions involved in the formation and stabilization of these adducts. The principle interaction common to all of the adducts is coulombic interactions between localized partial charges on the guest and the dipole of thiourea. Six classifications of disorder are described. The disorder of each guest is described and categorized. Assessment of the interactions in these adducts allows predictions of other adducts that should form with thiourea.

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HOST/GUEST ADDUCTS

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James Francis Fait

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APPROVAL

of a thesis submitted by

James Francis Fait

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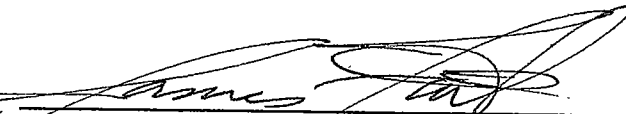

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ABSTRACT

Thiourea host/guest adducts display a variety of types of disorder of the guest molecules. As these adducts also exhibit dramatic selectivity in the guest molecules included in the adduct, models that accurately describe the disorder of the guest are required to assess the principle forces involved in the formation of these adducts. Crystallographic structural studies for eight adducts of thiourea have been completed and disorder models for each adduct have been developed. Thermodynamic data on two adducts was collected for assessing the magnitude of the interactions involved in the formation and stabilization of these adducts. The principle interaction common to all of the adducts is coulombic interactions between localized partial charges on the guest and the dipole of thiourea. Six classifications of disorder are described. The disorder of each guest is described and categorized. Assessment of the interactions in these adducts allows predictions of other adducts that should form with thiourea.

CHAPTER 1

INTRODUCTION

In molecular inclusion complexes, disorder is often observed because the interactions between the host lattice and the guest molecules are weak when compared to the stronger forces involved in other types of complexes.^{26,58} One group of molecular complexes, based on urea and thiourea, consists of an open lattice of the urea forming continuous channels throughout the crystal.^{25,28,58} In the thiourea adducts, the guest is located at particular positions along this channel, with the guest molecule disordered at these sites by any one of several mechanisms.²⁵ Thiourea forms host guest adducts with a wide variety of hydrocarbons, and the nature of the interactions involved in the formation of these adducts is of interest due to the selectivity of these adducts toward preferential inclusion of specific isomers in the host lattice.^{3,4,9,17} These adducts are similar to the adducts formed by urea with some organic compounds, but show a striking difference in the type of guest molecules that are accommodated.⁶³ The urea adducts preferentially complex with straight chain hydrocarbons and derivatives. Hydrocarbon derivatives with bulky side groups and rings

destabilize the urea adducts.⁶⁴ More bulky ring systems and substituted guest molecules are preferred for adduct formation with thiourea,^{3,17} with straight chain hydrocarbons included only when there are side chains or when the chain is long enough ($>C_{14}$) to form a helix with 5 carbons per turn in the channel.³⁴

Historical

Discovery of the Urea Adducts

The discovery of the urea adducts in 1940 was made accidentally when Bengen, while studying the effect of urea on proteins in pasteurized milk, encountered foaming problems and an emulsion that led him to add a small amount of n-octanol as a defrothing agent.¹⁰ Upon separation of the liquid, Bengen observed that long crystals had formed at the interface of the liquid layers. When Bengen attempted to reproduce the results, he observed that the crystals form when a saturated aqueous urea solution was mixed with n-octanol. Further investigations^{46,53,55,64,68,69} showed that the urea adducts selectively complex with the straight chain hydrocarbons. Branched and/or cyclic compounds were not included in the crystal unless the straight portions of the complex were long enough to overcome the destabilizing effect of the bulky side groups.

Discovery of the Thiourea Adducts

The thiourea adducts were discovered independently by Angla in France (1947)^{3,4,5} and Fetterly in the United States (1950).^{17,18} Fetterly became aware of the urea adducts through the Technical Oil Mission reports in 1946. He was attempting to improve the octane rating of gasoline by complexing the low octane branched paraffins. Urea would not serve for this purpose, but it was soon discovered by Fetterly that thiourea did complex with isoparaffins as well as naphthenes, some polyhalogen hydrocarbons, and alcohols and ketones derived from these compounds.^{45,56} Angla reported complexation of the terpene, camphene, cyclohexyl, and chloroparaffin classes (Figure 1).⁵ Fetterly proposed that a "supported hydrogen bond" was responsible for the existence of these adducts.

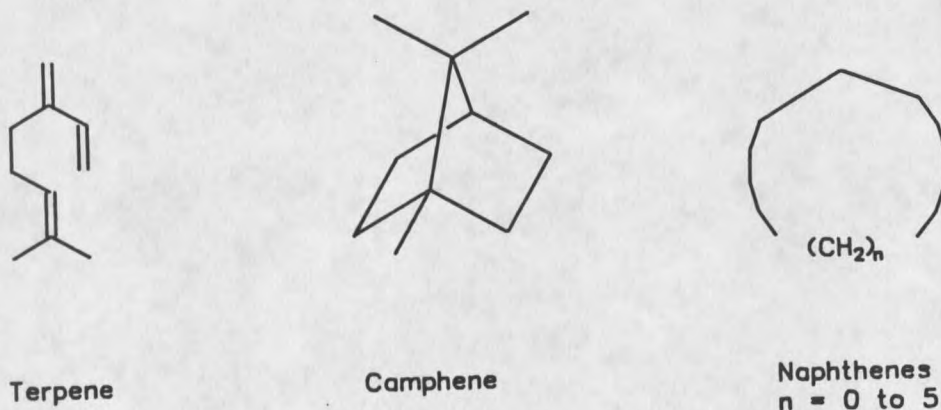


Figure 1. Examples of classes of compounds that form adducts with thiourea.

The supported hydrogen bond is defined as a hydrogen bond that is stabilized in a geometry that does not occur without the support of a channel or cavity by weak nonbonded interactions.¹⁹ Fetterly also established complex formation with the related compounds selenourea and tellurorea.¹⁸

Induced Adduction

Induced adduct formation is defined as adduct formation by a guest that does not normally form a stable adduct with the host, but is induced to form an adduct by the presence of another guest that often forms a stable complex with the host. Both the urea and thiourea host/guest complexes show induced adduct formation.^{21,55} Since the second guest, or inductor, initiates and stabilizes the host structure, otherwise unstable complexes can be formed. Application of induced adduction to the C₉ alkylbenzenes with thiourea by McCandless^{29,30,31} gave a broader range of complexes for use in extractive crystallization.

Structural Studies on Adducts of Urea and Thiourea

Lenne, as part of his initial characterization of the thiourea adducts, reported some initial work on the crystal structure of the cyclohexane thiourea adduct.²⁸ He established the basic orientation of the thiourea in the

structure, and established the existence of a channel in which the guest molecules were disordered. He did not attempt to depict the guest disorder, but did locate the general location of the guest within the channel near the sulfurs of the thiourea. Subsequent x-ray analysis of a number of urea and thiourea adducts by Smith⁵⁸ and Schlenk⁵⁵ confirmed this, as well as investigating the structure of the urea adducts. All of these determinations indicated that the guest molecule was disordered, and the host lattice was nearly invariant with respect to the guest. Space group indications for the thiourea show it to be rhombohedral, space group $R\bar{3}c$, with cell dimensions of $a = b = 15.8\text{\AA}$, $c = 12.5\text{\AA}$ (hexagonal indexing). The urea adducts form in the hexagonal space group $P6_12$, with cell dimensions $a = b = 8.230\text{\AA}$, $c = 11.005\text{\AA}$.⁵⁸ The urea molecules form a spiral around the linear hydrocarbon guest located parallel to the c axis, with the environment of the guest quite uniform along the length of the channel.⁵⁸ The channel of the thiourea structure is also parallel to the c axis, however there are planes defined by three thioureas with the sulfurs directed into the channel, unlike the urea adducts.⁵⁶ Based on the strong dipole moment of thiourea and the observations of Lenne, Schlenk proposed that the guest should be located in this region of maximum interaction. These regions of maximum interaction

occur at $c/2$ intervals, giving an interplanar spacing of 6.25Å.

Other Properties

Redlich(1950)^{45,46} contributed to the growing knowledge of the thiourea adducts by conducting a series of thermodynamic studies on several of the adducts. Using Gibbs free energy relationships and representing adduction by a chemical equilibrium, he reported that these adducts appear to form equilibrium systems much as in normal chemical reactions. Redlich reported the composition and equilibrium constants for the decomposition of the thiourea complexes of various isoparaffins, naphthenes, and carbon tetrachloride. The equilibrium constants for the adducts showed no trend with mole fraction of guest or with the size of guest.

Schiesser and Flitter(1952)⁵² attempted to correlate the structure and the ability of a given guest to form a complex. Their work concentrated on a prediction of the channel size, and predicted adduct formation based only on guest size. This concept is in accordance with Fetterly's supported hydrogen bond,^{19,52} but fails to predict the effect of inductors and the differences in selectivity between similar molecules when in adducts, especially those with conjugated systems and aromatic centers.

McLaughlin³³ compiled a comparison list of organic compounds of similar size and shape that either form or do not form complexes with thiourea. One example of this is benzene. Although the dimensions of the benzene ring are similar to those of cyclohexane, no adduct is formed. This suggests that more is involved in the adduct formation process than having a guest molecule of the right cross sectional dimensions. He also reported the formation of thiourea adducts with long chain ($>C_{14}$) n-paraffins, which form when the chain is long enough to form a helix in the thiourea channel with 5 methylene units per turn.

Extractive Crystallization

McCandless^{29,30,31,32} developed extractive crystallization as one use for the thiourea adducts, and in his research on this process, concluded there was more involved in formation of these adducts than just having the right sized molecule to support the channel. Extractive crystallization, much like distillation, can be used to separate one compound from another. The utility is, however, that the equilibria governing adduct formation are not the same as those governing distillation, giving rise to a variety of new separations that are not feasible by distillation. This technique is enhanced by the use of inductors, chemicals that alter the selection rules for adduct formation utilizing induced adduction. This allows

the separation of isomers that might otherwise be extremely difficult to separate.

Related Substances

Gas Hydrates

Water forms host guest complexes of several types with a variety of gases and small molecules.⁶⁰ These hydrates form complexes with varying stoichiometry depending in part on the formation conditions, but also have a limiting value dependent on the size of the included molecule.⁴¹ The hydrates have a significantly different structure from that of hexagonal ice,¹² and many of these complexes have melting points significantly above that of pure water,⁶⁰ indicating that the guest is stabilizing the lattice of the complex.

β -Quinol

Quinol forms stable adducts with many simple gases, including several of the noble gases.^{38,39,40,42,43} The quinol structure, like that of the gas hydrates, is quite open, allowing for a variety of small molecules to be incorporated in the structure.³⁸ This system forms a cage around the guest, trapping it in a void in the lattice. Free rotation of the guest is often observed, indicating that the guest is not involved in any strong interactions with the quinol host lattice. Magnetic data on the O₂

quinol clathrate indicates that the guest molecules are isolated from each other, allowing investigations of properties that are inaccessible in the pure substance.¹⁵

Cyclodextrins and Amylose

The cyclodextrins complex with a wide variety of organic substances, principally by incorporation of hydrophobic sections of the molecule inside the cyclodextrin.⁶² There is some channel character implicit in the cyclodextrin by nature of the molecular structure, and cyclodextrins exhibit host/guest interactions in solution as well as in the solid state.⁵⁴ The guest molecule in the cyclodextrin complexes is usually disordered, even at low temperature.⁶² These complexes are selective only on geometric and hydrophobic bases. The cyclodextrins are related to the amylose complexes that form with nonpolar hydrocarbons and iodine. The familiar starch indicator for I_2 and the adducts formed by amylose with linear hydrocarbons are closely related, with the amylose forming a helix with six sugars per turn, and the guest molecule occupying the resulting channel in the crystal.^{8,35,48,49,50,51}

Other Host Systems

Tri-o-thymotide

Tri-o-thymotide forms host/guest adducts with a variety of substances including alkanes and derivatives of

alkanes.^{27,37,44} Two types of complex are formed, depending on the size of the guest molecule. For the smaller molecules, a cage type structure is formed that will accommodate molecules up to 9.5Å. If the molecule is longer than this, a channel structure is formed, where the ratio of host to guest need not be rational. Some of the channel forms of this host display one dimensional scattering characteristic of disorder in the guest region of the structure.²⁷

Triphenylmethane

Triphenylmethane includes benzene, pyrrole, thiophen, or aniline as a molecule of crystallization.²³ 4,4'-Dihydroxytriphenylmethane and its derivatives, however, include a variety of hydrocarbons as guest molecules.⁶ Based on the sizes of the guest molecules, the host lattice appears to have a diameter of at least 6.5Å. Aromatics also complex with the dihydroxytriphenylmethane derivatives, but form a different type of complex than the channel form observed with the aliphatic complexes.⁶

Cyclotriphospazenes

The related series of cyclotriphosphazenes, tris(1,8-naphthalenedioxy)cyclotriphosphazene, tris(2,3-naphthalenedioxy)cyclotriphosphazene, and tris(o-phenylenedioxy)cyclotriphosphazene, all form host guest adducts with a wide variety of compounds.^{1,2} Some

of the host/guest systems exhibit preferential inclusion of one component of binary mixtures of guests.² Disorder is evident in several of these adducts, as is a nonstoichiometric ratio of host to guest.

N,N' Ditritylurea and Related Compounds

These hosts are characterized by a long molecular axis with rigid, bulky terminal groups.²² These groups prevent close packing, resulting in open pockets in the structure that can entrap any molecule of an appropriate size to fit in the pocket. In the case of the N,N' ditritylurea, polar molecules can be accommodated, with hydrogen bonding occurring when possible to the urea moiety of the host molecule.

Zeolites

The zeolites are naturally occurring and synthetic aluminosilicates with cation exchange properties, and when dehydrated, molecular sieve and sorptive capabilities.⁷ These properties arise because the dehydrated lattice of the zeolite is traversed by channels of molecular dimensions which are too narrow to accommodate some molecules, but narrow enough to contain others. This allows for the exchange of cations, as well as the molecular absorption character of these minerals.

Research Objectives

The objectives of this research are to determine the structures of a series of thiourea adducts, and to obtain crystallographic models of the disordered guests. Classification of the types of disorder, discerning some of the major interactions governing the host/guest interactions, and prediction of other guests that will form adducts with thiourea should follow from the models of the guest disorder.

CHAPTER 2

CARBON TETRACHLORIDE THIOUREA (1:3) ADDUCT

The first structure attempted in this project was that of the carbon tetrachloride thiourea adduct. In realization of the previous reports of serious disorder in these adducts, it was hoped that this simple molecule could be either ordered or be simple enough in its disorder to be easily characterized. In addition, the electron rich chlorine in the structure might enable a clearer picture of what was happening in the guest site than had been obtained to this point. To help minimize the effects of the adduct's instability and disorder, low temperature intensity data was collected at 170K.

ExperimentalCrystal Preparation

Reagent grade thiourea, methanol, and carbon tetrachloride were purchased from the J. T. Baker Chemical Company. Carbon tetrachloride was allowed to diffuse into a saturated solution of thiourea in methanol at room temperature ($\approx 25^{\circ}\text{C}$) and good quality crystals appeared in about 24 hours. An experimental density was obtained by flotation in chloroform/heptane solutions.

$D_o = 1.42(2) \text{ gcm}^{-3}$ (298K), $D_c = 1.433 \text{ gcm}^{-3}$ (170K), and $M_r = 382.17$. The adduct is unstable in air, as the crystals decompose through the loss of carbon tetrachloride through evaporation, resulting in a white microcrystalline powder. The crystal used for intensity data collection was mounted and sealed in a Lindemann glass capillary tube. Crystal dimensions were $\approx 0.5 \times 0.5 \times 1.0 \text{ mm}^3$.

Data Collection

Intensity data were collected on a Nicolet R3ME four circle diffractometer using the omega scan technique. The temperature of the crystal was maintained at 170K with a cold nitrogen stream supplied by a Nicolet LT-1 liquid nitrogen low temperature system. Three standard reflections were measured periodically throughout the course of the data collection to monitor crystal alignment and/or deterioration. There was no decrease in the standards over the course of the data collection; the maximum variation from the average was less than 3%. A total of 3531 reflections were collected, of which 1017 were unique and 640 were considered observed at the $6.0\sigma_F$ level ($R_{\text{merg}} = 0.033$). σ_F was calculated from counting statistics. Lattice parameters were obtained from the least squares fit to 12 reflections for which $8.5^\circ < 2\theta < 25.5^\circ$. Unit cell dimensions, space group designation and

other details of the data collection, structure solution, and refinement are included in Table 1.

Table 1. Experimental Data for Carbon Tetrachloride Thiourea Adduct

Formula	CCl ₄ ·3(SCN ₂ H ₄)	
Cell Dimensions	a=b	15.539(4)Å
	c	12.529(9)Å
Space Group	R3	
Cell Volume	2620.0(20)Å ³	
D _m	1.42(2) gcm ⁻³	
D _c	1.433 gcm ⁻³	
Crystal Dimensions	0.5 x 0.5 x 1.0 mm ³	
sin θ / λ _{max}	0.5944 Å ⁻¹	
Range	h	0 to ± 19
	k	0 to 19
	l	0 to ± 15
Total Reflections	3531	
Unique Reflections	1017	R _{merg} = 0.033
Observed Reflections	640	6 σ _F cutoff
Number of parameters refined	83	
R =	$\frac{\Sigma(F_O - F_C)}{\Sigma F_O }$	0.043
R _w =	$\frac{\Sigma(F_O - F_C)w^{\frac{1}{2}}}{\Sigma F_O w^{\frac{1}{2}}}$	0.033
S =	$\frac{\Sigma(F_O - F_C)w^{\frac{1}{2}}}{(m-n)^{\frac{1}{2}}}$	1.997

Data Reduction, Structure Solution,
and Refinement

The data were reduced in the usual manner with appropriate Lorentz and polarization corrections. Scattering factors for S, Cl, N, C, H and anomalous scattering terms for S, Cl, N, and C were taken from the International Tables for X-ray Crystallography;²⁴ all atoms were assumed to be in the zero ionization state. No correction for absorption was made as the crystal was enclosed in a capillary preventing indexing of faces and the low temperature apparatus would not allow collection of psi scan data.

An initial model was obtained by direct methods utilizing the Nicolet program package,⁵⁷ the XTAL system of crystallographic programs,⁶¹ and programs written locally. The S, C, and N atoms of the thiourea lattice structure were refined with anisotropic thermal parameters by full matrix least squares minimizing $\sum w(|F_o| - |F_c|)^2$ with all parameters refined in each full matrix block. Thiourea amino hydrogen position coordinates, determined from a difference Fourier electron density map at an intermediate stage of refinement, were refined along with isotropic thermal parameters. The weighting scheme used in the latter stages of refinement was $w = (\sigma_F)^{-2}$. A final difference Fourier electron density map showed maximum peak heights of $\approx 0.30 \text{ e}/\text{\AA}^3$ in the vicinity of the chlorine atoms in the channel with the

most negative peak $\approx -0.25 \text{ e}/\text{\AA}^3$. The largest shift over error value was less than 0.02 at convergence. The R for all of the data was 0.087, and the R for the observed data was 0.043. No corrections for secondary extinction were made or refined.

Disorder Model

Figure 2 illustrates the structure of the carbon tetrachloride thiourea adduct and the substantial disordering of the carbon tetrachloride molecule in the channel. The initial and final models for the carbon tetrachloride molecule are illustrated in Figure 3. Due to the substantial disorder of the system, obtaining a model for the carbon tetrachloride that made chemical sense was not a trivial problem. The initial model, derived by refining peaks located on difference Fourier electron density maps, suggested the final, simplified model with three anisotropic chlorine atoms representing the tetrahedral carbon tetrachloride. In the final model, the carbon tetrachloride is represented by an approximately tetrahedral carbon tetrachloride molecule with the carbon atom on the 3-fold axis and one of the molecular 2-fold axes normal to the 3-fold axis in the plane of the three thiourea sulfur atoms and approximately along a thiourea C-S vector. All atoms of the carbon tetrachloride were refined anisotropically with carbon to chlorine bond distances

