THE STRUCTURES OF THALLIUM TRIHALIDE COMPLEXES

by

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CHAPTER I

INTRODUCTION

I.1. Chemistry of Thallium

In 1861 W. Crookes(1), during his observation of the spectra of slimes from the sulphuric acid industry, detected a green line (λ 535 mμ) which did not correspond to any of the previously known elements. Further study of this substance led to the discovery of a new element which he called thallium. In 1862 A. Lamy isolated for the first time a fairly large quantity (14 g.) of thallium from the sulphuric acid industry slimes. From this he prepared several compounds of thallium, established its metallic mature and the similarity between its compounds and those of lead, silver and the alkali metals.

Thallium is a silvery-white soft metal with a high density (11.85 g. cm^{-3} at 20°), m.p. 303°; b.p. 1457°. It oxidises in moist air, decomposes steam at red heat and dissolves readily to form thallous compounds in dilute mineral acids other than HCl because of the insolubility of $TlCl$.

Unlike elements such as copper, zinc and others, thallium forms no characteristic minerals. It occurs mainly as an impurity in various minerals such as pyrite, chalcopyrite and zinc blende and when these are roasted, thallium oxides are evolved together with sulphuric dioxide which then accumulate and from which thallium is obtained.

Thallium, like the elements of the third group, combines with a maximum valency of +3. The R_2O_3 oxides lose

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their acidic properties and become basic on going from boron to thallium. Thallium (III) hydroxide is a weak base which acts as an acid at very high concentrations of NaOH to form thallates. The solubility of $R(OH)_3$ in water decreases on going from boron to thallium.

Although there is a similarity between thallium and the other elements of group III, there are also essential differences shown mainly by the existence of compounds of thallium (I). Sidgwick was the first to recognise this tendency which he ascribed to the presence of the inert electron pair.

Many of the compounds of thallium (I) are analogous to the corresponding compounds of the alkali metals. This can be attributed to the fact that the alkali and thallium cations have the same valency and very similar ionic radii. Thallium compounds are therefore isomorphous with the corresponding compounds of the alkali metals and often form mixed crystals with them. The similarity between thallium (I) and the alkali metals can be illustrated for instance by the considerable solubility of TlOH in water (25.9 g. per 100 ml water at 0^{o})(3). Thallium forms precipitates with many of the reagents for K^+, Rb^+, and Cs^+ e.g., chloroplatinate, cobaltnitrite, hexanitrodiphenyl amine and polinitrophenols.

Unlike the alkali metals, thallium forms other sparingly soluble compounds analogous to those of the monovalent cations of the heavy metals of group IB (Cu^+, Ag^+, Au^+) and to those of its nearest neighbours (Hg_2^{2+}, Hg^{2+}, Pb^{2+}). Thallium and these elements form sulphides, iodides, chromates, molybdates etc. which are sparingly soluble in water. Because the thallium (I) halides are photosensitive, there is a certain analogy between their properties and those of the corresponding salts of Ag^+ and Au^+

I.2. Complexes of Thallium (III) with organic amines

Little information is available at present on the stereochemistry of thallium (III) complexes and previous studies have been mainly concerned with their preparation and stoichiometry. The study of complex compounds of trivalent thallium with organic amines was initiated by Meyer(4) who first isolated complex thallium chlorides with pyridine, mono-, di- and triethylamine hydrochlorides. Renz repeated some of Meyer's syntheses and first obtained complex thallium chlorides with quinoline and atropine and with β-naphthylamine hydrochlorides. By double decomposition of thallium chloride aminates with potassium iodide he also synthesised some thallium iodide aminates. Hieber and Sonnekalb studied the reactions of thallium halides with ethylene diamine and showed that the chloride can combine with one, two or three molecules of ethylenediamine, the bromide with one or two molecules and the iodide with only one. Although a number of complex thallium aminates have already been prepared, their structures have been deduced exclusively by analogy with the corresponding compounds of gold, iron, platinum and other metals. For example, by analogy with cobalt, rhodium and iridium aminates Grinberg considers $TlCl_3(C_5H_5N)_3$ to be a complex with a coordination

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number of six; $[Tl(C_5H_5N)_3Cl_3]$.

In 1951 Sutton$^{(5)}$ reported the preparation of $TlbipCl_3$ and $TlphenCl_3$ where phen = 1,10-phenanthroline and bip = bipyridyl. These complexes were prepared by the addition of the appropriate ligand to an aqueous solution of thallic ion. Similar bromide and thiocyanate complexes were obtained by double decomposition of the complexes with potassium bromide and potassium thiocyanate.

Sutton$^{(6)}$ further investigated the bipyridyl and phenanthroline complexes together with the ethylenediamine complexes $TlBr_3$.en and TlI_3.en. From conductivity and ionic weight determinations in nitrobenzene of the thallic complexes of the type TlX_3L (L = ligand), he showed that they are dimeric electrolytes $[TlX_2L_2]^+[TlX_4]^-$, while those of the type $[TlX_2L_2]^+[X]^-$ were obtained when ethylenediamine was used as ligand. The only compounds of this type with bipyridyl or phenanthroline which were isolated were the iodides. The presence of $[TlX_4]^-$, ions was confirmed by precipitation with triphenylarsonium cation.

The growing interest in the coordination compounds of thallium (III) has recently been emphasised by the publication of several papers$^{(6 - 14)}$ from 1959 onwards on this subject. Methyl cyanide is widely used as a solvent in inorganic preparations and provides a route to a variety of new complexes of thallium (III) halides. Oxidation of thallium (I) chloride and bromide with halogens in methyl cyanide solutions gives quantitative yields of the appropriate thallium (III) halide. Mixing methyl cyanide solutions and the ligand L resulted

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in the precipitation of the complex with stoichiometry of the type TlX_3L_2, where X = Cl of Br and where L represents

a) a unidentate ligand such as pyridine, γ-picoline, morpholine or dimethyl sulfoxide (DMSO) or triphenylphosphine oxide,

b) half of a bidentate such as 1,10-phenanthroline (phen), 2,2'-bipyridyl (bip) or ethylenediamine (en).

Cotton(8) and co-workers prepared a series of salts of the type $MTlX_4$ where X = Cl, Br of I, and M is a large univalent cation such as the quaternary ammonium or arsonium ion. The $[TlCl_4]^-$ compounds are white, the $[TlBr_4]^-$ compounds are white or cream and the $[TlI_4]^-$ compounds are orange in colour.

Some structural features of $[TlX_4]^-$ ion have been determined by means of X-ray studies. Cotton found that $[(C_6H_5)_4As][TlCl_4]$ is isomorphous with $[(C_6H_5)_4As][FeCl_4]$. The latter is known, from a complete single crystal X-ray structure determination(15), to contain tetrahedral $[FeCl_4]^-$ ions. It is therefore extremely likely that the thallium compound contains tetrahedral $[TlCl_4]^-$ ions.

As a guide to the structure and stereochemistry of the complexes, conductivity(9, 16, 17) and molecular weight measurements have been carried out. The number of ions formed when a complex compound dissociates can often be determined by measuring its electrical conductivity in nitrobenzene solution, although the Werner-Miolate rule does not hold for all non-aqueous solvents

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since ions tend to associate even in dilute non-aqueous solutions to an extent which depends on the solvent and the solute(18). It is nevertheless assumed that a molar conductance of about 15 - 35 ohm^{-1} cm^{2} for solutions containing about 10^{-3} mole of solute per litre indicates the formation of two ions.

Kul'ba(16) performed structural studies by measuring electrical conductivities in nitrobenzene as the compounds of thallium (III) halide with 2,2'-bipyridyl and 1,10-phenanthroline are sparingly soluble in water and undergo extensive hydrolysis. No unambiguous conclusions could be drawn from these experiments regarding the number of ions formed by dissociation in nitrobenzene. It was however found that the dissociation of thallium (III) chloride in nitrobenzene is less than that of iron (III) chloride.

As a result of their appreciable dielectric constants, many salts behave as strong electrolytes in methyl cyanide. 1:1 and 1:2 electrolytes usually have molar conductivities in the ranges 120 - 160 and 220 - 280 ohm^{-1} cm^{2} respectively, for solutions containing about 10^{-3} mole of solute per litre.

Electrolytes generally have higher conductivities in methyl cyanide than in nitrobenzene or nitromethane and the former solvent is therefore to be prefered. All three solvents however suffer from the disadvantage that they may cause solvolysis which could lead to spurious conductivity data. For example small conductivity values ($\Lambda_m \sim 30$ ohm^{-1} cm^{2}) in methyl cyanide are usually

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indicative of an equilibrium of the type

$$MX_NL + MeCN \rightleftharpoons [MX_{N-1}.L,MeCN]^+X^-$$

With the exception of $TlCl_3(DMSO)_2$ all the complexes of the type TlX_3L_2 are virtually insoluble in nonpolar solvents such as benzene, pentane and chloroform.

Most of these complexes were sufficiently soluble in methyl cyanide for conductivity measurements to be made. Significant conductivity values were observed although the values of Λ_m calculated for the monomeric formulations were less than those usually found for 1:1 electrolytes.

The formulation of the compounds of the stoichiometry $M[TlX_4]$ as uni-univalent electrolytes is substantiated by their molar electrolytic conductances in CH_3CN which are in the range of 130 - 170 ohm^{-1} cm^2 mole^{-1} (8).

The compound prepared by the reaction of pyridine with aqueous thallic chloride was reported as $TlCl_3(C_5H_5N)_3$. Kul'ba and co-workers(9), however, claimed that the product of this reaction is in fact $TlCl_3(C_5H_5)_2$ and this stoichiometry was confirmed by Cotton(8). The molar conductane of this compound is 107 ohm^{-1} cm^2 mole^{-1} and indicates that the compound may be ionic. This value is somewhat low for the formula $[Tl(C_5H_5N)_2Cl_2]^+[Cl]^{-1}$ but a little high for the formula $[Tl(C_5H_5N)_4Cl_2]^+[TlCl_4]^-$ since on this basis the molar conductance should be 214 ohm^{-1} cm^2 mole^{-1}.

The conductivity of $TlCl_3$(phen) in methyl cyanide was found to be 52 ohm^{-1} cm^2 mole^{-1} for the formula $TlCl_3$(phen) or twice that for a dimer. The latter value of 104 ohm^{-1}cm^{2}mole^{-1} is only a little below that for the ionic formula [Tl(phen)$_2$Cl$_2$][TlCl$_4$], whereas the former is only one-third of that which would be expected for [Tl(phen)Cl$_2$][Cl].

Trichlorobis(dimethyl sulfoxide) thallium (III), TlCl$_3$(DMSO)$_2$, is believed to be nonionic and its conductivity is 216Λ_m. This may arise from an anionic dissociation of type$^{(20)}$.

$$TlX_3L_2 + CH_3CN \rightleftharpoons TlX_2(CH_3CN)L_2 + X^-$$

Such behavior is often observed in polar solvents. The solid compound is very likely to posess a dimeric structure with halogen atom bridging it.

The coordination of DMSO to thallium through the oxygen is demonstrated by the infrared spectrum of the solid, which shows that the S-O stretching mode shifts to 930 cm^{-1}. This is typical for complexes containing O-coordinated DMSO.

All these results for the TlCl$_3$(DMSO)$_2$ complex indicate that an authentic five-coordinated Tl (III) complex is likely. X-ray structure analysis is probably the only method which can indisputably prove or disprove the existence of five-coordinated monomers in the solid state.

Electrolysis experiments were carried out by Kul'ba and co-workers$^{(17)}$ to identify the anionic or cationic function of the complex halides of tervalent thallium. The deposits on the electrodes were analysed and each found to contain both thallium and halogen. Consequently both types of ion contained both species during the

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electrolysis. The following structure was then proposed.

$[TlX_2L_2][TlX_4]$

If this structure is correct, strong structural similarities between the complexes of tervalent thallium pyridine, 2,2'-bipyridyl, 1,10-phenanthroline and ethylenediamine exist.

Vibrational spectroscopy has not been extensively employed in the study of complexes such as $TlX_3(py)_2$ and TlX_3(chelate). In two recent articles (13, 20) the authors assigned the broad band, observed at about 292 cm^{-1}, to the thallium-chloride stretching vibration in the tetrahedral $TlCl_4^-$ ion.

McWhinnie(13) found that the infrared spectrum supported the presence of the $TlCl_4^-$ ion in acetone solution of $TlCl_3(py)_2$. He assigned the single band located at 381 cm^{-1} to the thallium-chlorine stretching frequency of the cationic species. The solid state spectrum is very different from that in acetone. On this evidence it appears unlikely that the solid state structure is based on the ionic units existing in the acetone solution.

The absence of bands associated with the TlX_4^- ion from $TlX_3(DMSO)_2$ suggests that structures of the type $[TlL_4X_2][TlX_4]$ are not present. The solid state spectrum of $TlCl_3$ (chelate) is difficult to interpret and it can only be remarked that similar spectra of the compounds $TlCl_3$ (chelate) imply similar solid state structures.

These investigations further emphasise the urgent need for at least one complete crystal structure determination.

/Discussion..

Discussion

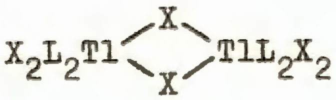
Published data providing definite structural information on thallium (III) complexes is very limited. Far infrared spectroscopy is ideally suited to the structural study of molecular addition compounds of heavy-metal halides because it enables characteristic groupings of elements to be rapidly identified. This region of the spectrum has only recently become accesssible and, as other techniques are either more tedious or less reliable, little information is available on the structures of these compounds.

The group of compounds of Tl(III) halides with neutral ligands, dimethyl sulfoxide, triphenylphosphine oxide, pyridine and 1,10-phenanthroline, pose some interesting problems in the assignment of structure. Unambiguous conclusions on the basis of the usual simple physical measurements are elusive, if not unattainable for several of them. These complexes are all of the stoichiometric type TlX_3L_2, where L represents a unidentate or half of a bidentate ligand.

In general the following five structural possibilities appear plausible for these compounds.

I TlX_3L_2
Five-coordinated monomer

II $[TlL_2X_2]X$
Ionic dimer

III 

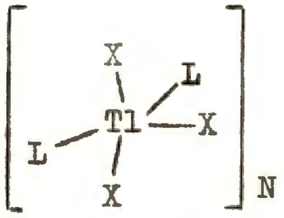
$X_2L_2Tl(\mu\text{-}X)_2TlL_2X_2$

Six-coordinated dimer

IV $[TlL_4X_2][TlX_4]$
Ionic dimer

/V.....

V



Infinite chain, six-coordinated

Both $TlX_3(C_5H_5N)_2$ and $TlCl_3$(phen) have ionic structure IV in solution as suggested by conductance data.

By contrast an essentially nonionic and monomeric structures are indicated for DMSO complexes. These could be genuine five-coordinated structures of type I. The species in solution might also be six-coordinated, monomeric structures resulting from solvent coordination, namely [$TlX_3(DMSO)_2$Solvent]. There is also the possibility that in the solid state six-coordinated dimers, III, might exist or chain polymers, V,which dissociate in solution to give

[$TlX_3(DMSO)_2$Solvent]

The available data suggest that the stereochemistry of thallium (III) is probably varied, complicated, and certainly very incompletely understood at present. The need for X-ray structural work is clearly evident.

The compounds TlX_3Am where Am stands for ethylenediamine, 1,10-phenanthroline, 2,2'-bipyridyl or two molecules of pyridine, and X = Cl, Br or I, have the structure [TlX_2Am][TlX_4] in solution. Their solid state infrared spectrum are similar and this implies similar solid state structures. It was therefore decided to make a detailed study of trichloro 1,10-phe-

/nanthro-..

nanthroline-thallium (III) using X-ray crystallographic methods.

I.3. Experimental

Chlorine gas was passed through a suspension of thallous chloride (1.2g) in methyl cyanide (10 ml). The reaction mixture was stirred and acidified to prevent the hydrolysis of the thallic ion. When all the solid was dissolved, the excess chlorine was removed with a fast stream of air. Ethanolic solution of 1 g 1,10-phenanthroline was added to the clear solution. The solution immediately became white in color. The product was separated by filtration, washed with cold ether and recrystallized from methyl cyanide.

The same procedure was repeated using 0.5 g. 2,2'-bipyridyl.

Analytical Data

Compound	Tl %		Cl %		N %	
	Found	Calcd	Found	Calcd	Found	Calcd
$TlCl_3$(phen)	41.59	41.62	21.65	21.66	5.86	5.71
$TlCl_3$(bip)	43.59	43.67	22.84	22.77	6.00	6.00

Compound	C %		H %	
	Found	Calcd	Found	Calcd
$TlCl_3$(phen)	29.81	29.35	1.65	1.65
$TlCl_3$(bip)	25.96	25.72	1.67	1.73

/CHAPTER II..

CHAPTER II

STRUCTURE DETERMINATION

The techniques used in the experimental part of this section, are standard crystallographic practice(21,22).

II.1. Crystal Data

The crystals were grown by slow cooling of a warm saturated solution of $TlCl_3$(phen) in methyl cyanide. Needle shaped crystals were obtained which were examined for flaws in a polarising microscope. The crystals exhibited oblique extinction in polarised light.

All X-ray photographs were taken with Ni filtered Cu K_α radiation. The preliminary oscillation, zero and first layer line Weissenberg photographs showed that the crystals belong to the triclinic system. Precession and zero-layer Weissenberg films were taken to determine the cell dimensions and the values obtained were subjected to a Delaunay reduction(23). The following dimensions were found:

$a = 9.44 \pm 0.02$ Å $\quad \alpha = 98.2 \pm 0.5^\circ$

$b = 10.94 \pm 0.02$ Å $\quad \beta = 96.6 \pm 0.5^\circ$

$c = 7.55 \pm 0.03$ Å $\quad \gamma = 115.9 \pm 0.5^\circ$

Cell volume = 680 Å

The density was determined using the flotation method and found to be 2.39 g cm^{-3} which agrees satisfactorily with the value of 2.40 g cm^{-3} on the basis of two molecules per unit-cell.

/II.2......

II.2. Intensity Photographs and Processing

The crystal chosen for collection of intensities was a needle with dimensions of 0.4, 0.08 and 0.1 mm which was mounted about [001]. (h,k,0) to (h,k,5) equi-inclination Weissenberg photographs were taken using the multiple film technique. A wide range of intensities is covered by this technique in which a pack of 6 films placed one behind the other is exposed to the diffracted X-rays. The intensity is reduced by absorption by a factor of about three per film. The exposure was kept constant at 48 hours for all layer lines.

The intesity of each recorded spot was visually estimated by comparison with a standard strip. A total of 2214 reflections was collected of which 14 were not observed. Before processing the measured reflection intensities, a value of one third of the minimum measurable value was assigned to all reflections which were too weak to be measured. This is in keeping with theoretical considerations for centrosymmetric crystals(24). The intensities measured on successive films were put on the same arbitrary scale using the program PB06 written by Dr. E.G. Boonstra for the IBM704 computer.

The Lorentz, polarization and spotshape corrections were applied using the computer program CORRECT written by Dr. E.G. Boonstra for the IBM 360/40 computer. The size of the specimen did not justify the application of absorption corrections.

/II.3....

II.3. Structure Determination

Patterson Synthesis

As electrons scatter X-rays, a crystal structure examined by X-rays may be regarded as a periodic three-dimensional distribution of electron density $\rho(x, y, z)$. In common with all three-dimensional periodic functions, the electron density can be represented by a three-dimensional Fourier series of the form$^{(25, 26)}$

$$\rho(x,y,z) = \sum_h \sum_k \sum_l \frac{F(hkl)}{V} \exp -2\pi i(hx/a + ky/b + lz/c) \quad ..(A)$$

where

$\rho(x,y,z)$ = electron density at the point (x,y,z)

(x,y,z) = fractional coordinates of a point in in the unit cell.

$F(h,k,l)$ = structure factor of the **reflection** (h,k,l).

It is convenient to write this Fourier series in the form

$$\rho(x,y,z) = \sum\sum\sum_{-\infty}^{+\infty} \frac{|F(h,k,l)|}{V} \cos\left[\frac{2\pi hx}{a} + \frac{2\pi ky}{b} + \frac{2\pi lz}{c} - \alpha(h,k,l)\right]$$

where $\alpha(h,k,l)$ = phase angle of the structure factor $F(h,k,l)$. In practice only $|F(h,k,l)|$ is observed, but a knowledge of the phase angles α is essential before the summation can be done. The phase angles are restricted to 0 or π for a centrosymmetric crystal.

This "phase problem" can be overcome by various methods of which the most convenient is the Patterson synthesis which allows the position of heavy atoms in a structure to be established. Phases are then calculated from the known heavy-atom positions and these are usually good enough to indicate the positions of the other atoms in a structure when used together with observed amplitudes in a Fourier summation.

The Patterson function P(u,v,w) is defined as

$$P(u,v,w)=\int_0^a\int_0^b\int_0^c \rho(x,y,z)\,\rho(x+u,y+v,2+w)dx\ dy\ dz$$

where the integration is over the whole unit cell. This may be reduced to

$$P(u,v,w)=\frac{1}{V}\sum_h\sum_k\sum_l |F(h,k,l)|^2\exp[2\pi i(hu+kv+lw)]$$

$$=\frac{1}{V}\sum\sum\sum I(h,k,l)\exp[2\pi i(hu+kv+lw)]$$

where I(h,k,l) are the observed intensities. This series can be summed without ambiguity for all space groups.

The function P(u,v,w) is of great value in crystal analysis as it can only attains a large value when both $\rho(x,y,z)$ and $\rho(x+u,y+v,z+w)$ have large values. This will occur when there are atoms situated at both (x,y,z) and (x+u, y+v, z+w) separated by the vector distance (u,v,w). A maximum in the function P(u,v,w) at (u_1,v_1,w_1) thus corresponds to an inter-atomic distance in the crystal defined by a vector whose components are u_1,v_1,w_1. The Patterson function can therefore be interpreted as a three-dimensional inter-atomic vector map in which the vectors from the origin to the maxima are the inter-atomic vectors. Because the peak heights are proportional to the products of the atomic numbers of the atoms concerned, the vectors between heavy atoms can usually

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easily be distinguished. If there are N atoms in the unit cell there will be N^2 Patterson peaks. Of these, N coincide with the origin, and a further N(N-1)/2 are related to the remaining N(N-1)/2 by a centre of symmetry. The Fourier coefficients of the Patterson synthesis are all real and this is the reason for there always being a centre of symmetry at its origin. This means that the symmetry of the Patterson function is equal to or higher than that of electron density.

The interpretation of a Patterson synthesis involves the use of symmetry elements of the unit cell. The inter-atomic vectors between symmetry - related heavy atoms may be isolated and identified. In a crystal which has a two-fold b-axis, an atom at (x,y,z) is accompanied by one at the equivalent (-x, y,-z). A peak of weight Z^2 (Z = atomic number) will be found in the Patterson function at (2u,o,2w) corresponding to a vector between the two equivalent atoms. The plane in which this vector, connecting symmetry related atoms, falls is the plane v = 0. Such a section is known as a Harker section.

All the intensities measured were used for the calculation of a three-dimensional Patterson synthesis using the centrosymmetric Fourier program written by Gantzel and Hope (U.C.L.A.) and modified for the use on the 360/40 IBM computer by Miss J. Hewitt.

A strong peak was observed at (0.34, 0.38, 0.52), which was interpreted as the Tl-Tl vector. From this the parameters of the thallium atom were obtained for

/use.....

use in the calculation of the trial structure. Three peaks of lesser intensity were assigned to the three Tl-Cl(1), Tl-Cl(2) and Tl-Cl(3) vectors. Since it was not certain whether the compound belonged to the space group P1 or P$\overline{1}$, an electron density map was calculated with only the thallium atom contributing to Fc.

The Fourier Synthesis

Equation A, mentioned above, may be written as follows for a centrosymmetric structure:-

$$\rho(x,y,z)=\frac{1}{V}\sum_{h}\sum_{k}\sum_{l}\pm\left|F(h,k,l)\right|\cos 2\pi(hx/a + ky/b + lz/c)$$

since the value of the phase angle is restricted to 0 or π .

When the position of a heavy atom is known and included in this summation, its contribution to the average structure factor will dominate that of the light atoms so that the phase will be correct in most cases. From successive Fourier and structure factor calculations initiated using only the heavy atoms in the trial structure, the position of the other atoms can be found. As the mayor portion of the structure amplitude is due to the heavy atom contribution, information concerning the light atoms must be derived from the residual of the structure amplitude. The accuracy of their determination thus is reduced. The presence of the heavy atom also causes a higher absorption coefficient and makes correction of the intensities more difficult.

The square roots of the corrected intensities that

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were used for the Patterson synthesis were used for the calculation of the electron density map phased only by the contribution of the thallium atom. The centrosymmetric Fourier program by Gantzel and Hope was again used for this computation. This three-dimensional electron density distribution map immediately showed the positions of all the remaining 17 atoms. The three chlorine positions indicated by the Patterson map were confirmed and the space group is thus definitely $P\bar{1}$.

Refinement

The refinement of the trial structure was done on the IBM 360/40 computer of the C.S.I.R. using the full matrix least squares program ORFLS of Busing, Martin and Levy.

The theory of least squares refinement is well known and is described in various texts(27). Basically this method changes the atomic coordinates of the trial structure in such a way as to improve the agreement between the observed structure factors (Fo) and the structure factors calculated from the trial structure (Fc).

The quantity minimized by the program ORFLS is $\Sigma\ w\ (|Fo|-k|Fc|)^2$ where w is the weight of a particular term and is inversely proportional to the square of the standard error in Fo. The program refines the scale factors, positional atomic parameters, the overall temperature factor and isotropic or anisotropic individual temperature factors as required.

The overall agreement between the observed and calculated structure factors is expressed in terms of the mean discrepancy

$$R = \frac{\sum_{hkl} \left(|Fo| - |Fc| \right)}{\sum |Fo|}$$

R is called the residual or reliability factor and is usually expressed as percentage.

Using all the observed intensities, the scale factor, the atomic coordinates and the individual isotropic factors were refined. The initial value of R was 35.5% but after a few cycles it dropped to 13%. Refinement was considered complete when all parameters shifts were less than one tenth of their estimated standard deviations.

The final atomic parameters and their estimated standard deviations are given in TABLE I. The observed (Fo) and calculated structure factors (Fc) are given in TABLE II.

TABLE I Fractional coordinates and isotropic temperature factors with standard deviations x 10^4 in brackets

	x	y	z	B(Å^2)
Tl	0.1721 (1)	0.1891 (1)	0.2128 (2)	1.89 (325)
Cl(1)	0.3314 (10)	0.2712 (9)	0.5223 (16)	3.29 (1670)
Cl(2)	0.0699 (10)	-0.0677 (9)	0.1766 (15)	3.20 (1632)
Cl(3)	0.3701 (11)	0.2416 (9)	0.0189 (16)	3.6 (1809)
N(1)	-0.0692 (30)	0.1729 (27)	0.2700 (45)	2.58 (4866)
N(2)	0.1654 (27)	0.3996 (24)	0.1979 (40)	2.00 (4179)
C(1)	-0.1837 (35)	0.0580 (31)	0.3081 (54)	2.39 (5456)
C(2)	-0.3318 (44)	0.0500 (38)	0.3392 (60)	3.49 (7141)
C(3)	-0.3576 (39)	0.1691 (34)	0.3412 (58)	2.87 (6226)
C(4)	-0.2358 (38)	0.2876 (34)	0.3067 (57)	2.77 (6007)
C(5)	-0.2441 (41)	0.4204 (36)	0.3148 (60)	3.12 (6480)
C(6)	-0.1241 (34)	0.5338 (30)	0.2886 (50)	2.19 (5249)
C(7)	0.0198 (33)	0.5318 (28)	0.2420 (50)	1.94 (4852)
C(8)	0.1460 (38)	0.6482 (33)	0.2146 (57)	2.77 (5961)
C(9)	0.2846 (43)	0.6426 (38)	0.1818 (63)	3.44 (6980)
C(10)	0.2893 (39)	0.5140 (34)	0.1734 (58)	2.89 (6169)
C(11)	0.0355 (32)	0.4065 (28)	0.2373 (50)	1.93 (4888)
C(12)	-0.0945 (34)	0.2861 (30)	0.2765 (52)	2.15 (5197)

k	Fo	Fc
H 0, L 0		
2	107	-125
3	115	-115
4	43	35
5	99	95
6	40	36
7	55	-44
8	81	-79
9	51	-43
10	38	35
11	45	45
H 1, L 0		
2	65	-69
3	47	38
4	104	99
5	63	59
6	26	-22
7	72	-66
8	52	-46
9	24	29
10	42	47
11	5	-2
H 2, L 0		
0	92	-108
1	51	-57
2	16	10
3	47	52
4	100	107
5	6	4
6	80	-83
7	45	-51
8	31	33
9	53	56
10	6	-1
11	24	-42
H 3, L 0		
0	75	-80
1	37	-32
2	92	97
3	78	95
4	25	24
5	88	-92
6	40	-49
7	39	45
8	59	61
9	6	-0
10	30	-43
H=4, L=0		
0	72	-76
1	67	68
2	117	131
3	19	19
4	77	-90
5	53	51
6	39	42
7	55	66
8	6	8
9	24	-33
H=5, L=0		
0	51	53
1	102	118
2	7	3
3	73	-84
4	40	-52
5	39	49
6	40	48
7	11	16
8	20	-27
H 6, L 0		
0	87	94
1	8	-1
2	49	-61
3	38	-44
4	23	21
5	47	57
6	15	19
7	11	-16
H=7, L 0		
0	7	3
1	65	-82
2	24	-34
3	7	11
4	35	44
5	24	29
6	4	-11
H 8, L=0		
0	42	-49
1	61	-64
2	7	-6
3	30	35
4	26	33
H 9, L=0		
0	51	-53
1	6	-11
2	27	32
3	22	29
H=10, L=0		
0	16	-14
1	21	31
H -1, L=0		
3	147	-167
4	153	-163
5	38	32
6	93	91
7	19	18
8	61	-60
9	83	-69
10	8	-4
11	51	47
12	38	35
H -2, L 0		
0	93	108
1	44	40
2	133	145
3	63	52
4	171	-164
5	134	-131
6	36	30
7	103	102
8	33	31
9	50	-48
10	60	-53
11	7	6
12	49	40
13	36	40
H= -3, L=0		
0	81	-80
1	55	-53
2	14	14
3	97	99
4	33	25
5	112	-107
6	105	-101
7	29	22
8	93	93
9	39	32
10	41	-42
11	50	-44
12	6	6
13	43	41
H -4, L 0		
0	84	-71
1	114	-111
2	37	-35
3	51	50
4	94	89
5	5	-0
6	127	-101
7	86	-70
8	51	39
9	103	87
10	37	39
11	54	16
12	48	39
13	5	3
H -5, L 0		
0	59	53
1	99	-91
2	100	-109
3	25	-23
4	80	80
5	80	73
6	14	-10
7	89	-73
8	51	-46
9	62	49
10	87	79
11	8	5
12	56	-38
13	44	-33
H -6, L=0		
0	93	94
1	59	50
2	83	79
3	105	-109
4	10	-9
5	90	84
6	89	77
7	41	-36
8	66	-66
9	34	-28
10	63	47
11	69	54
12	7	4
13	49	-40
H= -7, L 0		
0	7	3
1	72	66
2	47	40
3	67	-62
4	94	-92
5	7	-5
6	97	84
7	53	41
8	13	6
9	70	-65
10	25	-21
11	53	43
12	58	46
13	5	-4
H -8, L 0		
0	49	-49
1	8	12
2	64	67
3	37	31
4	55	-48
5	66	-64
6	18	14
7	83	73
8	79	67
9	34	-27
10	62	-55
11	21	-16
12	32	29
13	39	38
H= -9, L=0		
0	57	-53
1	32	-33
2	24	27
3	65	65
4	34	33
5	56	-48
6	57	-46
7	24	20
8	65	57
9	38	30
10	42	-30
11	56	-43
12	28	-23
H -10, L=0		
0	16	-14
1	45	-43
2	20	-20
3	37	33
4	66	62
5	7	6
6	53	-42
7	53	-40
8	21	18
9	59	47
10	10	11
11	37	-30
12	43	-40
H -11, L 0		
2	36	-37
3	16	-17
4	35	32
5	53	46
6	6	8
7	[illegible]	-43
8	10	-33
9	5	10
10	10	39
H 0, L=1		
1	139	-152
2	119	-111
3	33	32
4	116	134
5	82	75
6	68	-63
7	95	-94
8	37	-33
9	67	74
10	30	34
11	17	-20
H 1, L 1		
0	84	-95
1	100	-109
2	24	20
3	124	135
4	107	101
5	49	46
6	92	-96
7	7	4
8	24	29
9	38	44
10	11	-18
11	29	-34
H=2, L=1		
0	115	-124
1	4	4
2	111	124
3	93	92
4	14	-14
5	75	-78
6	17	-17
7	57	61
8	37	45
9	6	-4
10	34	-40
H=3, L=1		
0	36	-34
1	80	85
2	72	78
3	30	-28
4	70	-73
5	21	-23
6	51	58
7	50	55
8	12	9
9	29	-38
H=4, L=1		
0	71	74
1	83	98
2	28	-25
3	87	-94
4	43	-42
5	44	49
6	59	70
7	20	18
8	28	-36
H=5, L=1		
0	81	88
1	19	-25
2	89	-98
3	44	-51
4	30	32
5	52	63
6	17	15
7	20	-27
H=6, L=1		
0	12	-11
1	78	-86
2	48	-60
3	13	18
4	37	48
5	11	17
6	22	-32
H=7, L=1		
1	[illegible]	[illegible]
2	7	9
3	[illegible]	[illegible]
4	11	17
5	15	-28
H=8, L=1		
0	44	-60
1	12	16
2	33	40
3	17	27
4	11	-23
H=9, L=1		
0	6	-8
1	29	41
2	20	30
H=10, L=1		
0	28	42
H 1, L 1		
-1	94	93
-2	130	138
-3	48	41
-4	122	117
-5	128	-140
-6	5	9
-7	87	96
-8	54	54
-9	47	-50
-10	46	-47
-11	7	-10
-12	24	28
H=2, L=1		
-1	102	-112
-2	7	4
-3	102	109
-4	61	65
-5	147	-148
-6	112	-115
-7	21	21
-8	92	97
-9	44	46
-10	24	-38
-11	36	-41
-12	6	-3
-13	27	33
H-3, L 1		
-1	119	-129
-2	85	-85
-3	9	2
-4	99	109
-5	23	21
-6	52	-56
-7	86	-95
-8	32	29
-9	92	102
-10	42	43
-11	32	-40
-12	44	-45
-13	5	4
H=4, L=1		
-1	51	-53
-2	139	-142
-3	62	-57
-4	55	48
-5	99	100
-6	46	44
-7	52	-55
-8	67	-72
-9	21	12
-10	78	89
-11	31	37
-12	36	-40
-13	42	-48
H=5, L=1		
-1	64	67
-2	93	-92
-3	97	-93
-4	26	-24
-5	86	88
-6	83	76
-7	25	19
-8	55	-52
-9	48	-49
-10	32	22
-11	55	63
-12	21	24
H=6, L=1		
-1	80	88
-2	64	69
-3	32	-38
-4	108	-104
-5	6	4
-6	113	112
-7	59	62
-8	7	-8
-9	58	-54
-10	38	-35
-11	19	15
-12	41	41
-13	5	12
H=7, L=1		
-1	7	-2
-2	79	86
-3	64	76
-4	34	-37
-5	86	-86
-6	17	13
-7	67	62
-8	60	55
-9	38	-34
-10	55	-56
-11	29	-26
-12	15	16
-13	26	31
H 8, L=1		
-1	33	-37
-2	8	7
-3	60	66
-4	60	62
-5	37	-36
-6	70	-82
-7	22	-20
-8	71	72
-9	48	46
-10	36	-31
-11	65	-57
-12	24	-15
-13	22	24
H-9, L=1		
-1	34	-37
-2	23	-29
-3	7	12
-4	56	63
-5	38	34
-6	38	-32
-7	62	-63
-8	7	-10
-9	65	57
-10	38	36
-11	31	-30
-12	43	-43
-13	3	-13
H-10, L=1		
-1	5	-9
-2	32	-39
-3	19	-23
-4	34	34
-5	36	42
-6	16	16
-7	35	-34
-8	56	-51
-9	6	-5
-10	46	43
-11	26	27
-12	3	-21
H-11, L=1		
-3	27	-40
-4	14	-17
-5	26	25
-6	29	32
-7	5	3
-8	28	-12
-9	30	-33
-10	4	0
H= -1, L=1		
2	81	-68
3	68	-64
4	13	11
5	142	127
6	66	59
7	69	-64
8	100	-89
9	8	-3
10	41	58
11	32	31
12	14	-21
H= -2, L 1		
1	166	162
3	93	-78
4	98	-80
5	72	63
6	72	63
7	43	33
8	73	-55
9	96	-84
10	7	-8
11	61	53
12	29	34
H= -3, L=1		
1	146	132
2	145	139
4	143	124
5	68	-55
6	17	18
7	70	59
8	12	12
9	50	-43
10	66	-60
11	7	-1
12	59	47
13	27	31
H= -4, L=1		
1	45	-41
2	168	158
3	114	104
5	173	-154
6	61	-46
7	64	52
8	75	63
9	7	6
10	53	-49
11	39	-38
12	6	7
13	46	44
H= -5, L=1		
1	114	-105
2	26	-23
3	72	66
4	119	103
6	154	-141
7	53	-42
8	77	68
9	71	61
10	8	-8
11	47	-40
12	26	-22
13	24	16
H -6, L=1		
1	56	-53
2	91	-93
3	59	-46
4	79	68
5	91	75
7	103	-87
8	37	-30
9	90	77
10	78	65
11	7	-8
12	53	-39
13	15	-16
H= -7, L=1		
1	7	-1
2	74	-65
3	72	-67
4	20	-16
5	74	60
6	77	59
8	96	-77
9	23	-18
10	77	61
11	66	57
12	6	-10
13	45	-41
H= -8, L=1		
1	65	57
2	7	-4
3	68	-60
4	62	-56
5	22	17
6	69	61
7	55	45
9	67	-59
10	17	-14
11	66	49
12	55	39
13	13	-12
H= -9, L=1		
1	41	38
2	66	61
3	8	1
4	79	-77
5	41	-36
6	38	30
7	63	54
8	33	27
10	51	-42
11	6	-6
12	41	32
H= -10, L=1		
1	32	-29
2	36	31
3	76	58
4	7	-6
5	62	-55
6	35	-27
7	50	36
8	71	52
9	6	10
11	40	-36
H -11, L=1		
1	32	-42
2	21	-20
3	28	28
4	63	52
5	6	2
6	65	-46
7	31	-29
8	36	30
9	50	41
10	10	8
H= -1, L=1		
-2	83	-80
-3	119	132
-4	51	-49
-5	67	68
-6	63	65
-7	34	-36
-8	45	-53
-9	33	-41
-10	29	30
-11	41	50
H= -2, L=1		
0	122	137
-1	28	-30
-2	114	-116
-3	32	-32
-4	50	57
-5	68	74
-6	19	-15
-7	61	-78
-8	41	-56
-9	21	26
-10	37	52
H= -3, L=1		
0	35	-35
-1	135	-125
-2	24	-18
-3	90	94
-4	81	90
-5	19	-5
-6	74	-87
-7	50	-55
-8	18	20
-9	42	51
-10	5	13
H -4, L=1		
0	116	-114
-1	44	-38
-2	82	83
-3	88	99
-4	19	19
-5	62	-69
-6	48	-56
-7	7	7
-8	42	47
-9	9	13
H= -5, L 1		
0	49	-41
-1	71	69
-2	98	98
-3	33	33
-4	49	-46
-5	47	-53
-6	13	17
-7	41	46
-8	13	18
H= -6, L=1		
0	30	27
-1	59	61
-2	38	45
-3	32	-37
-4	48	-49
-5	7	10
-6	46	53
-7	25	28
H= -7, L=1		
0	95	87
-1	18	16
-2	39	-40
-3	56	-62
-4	7	4
-5	45	53
-6	24	32
H= -8, L=1		
0	65	56
-1	39	-48
-2	63	-60
-3	6	-3
-4	39	47
-5	19	31
H= -9, L=1		
0	38	-41
-1	55	-57
-2	6	-7
H= -10, L=1		
0	49	-48
-1	5	-10
H=0, L=2		
1	59	-65
2	4	2
3	154	151
4	110	98
5	73	-66
6	98	-86
7	25	20
8	72	79
9	42	44
10	30	-29
11	43	-45
H=1, L=2		
0	195	-267
1	9	-4
2	120	138
3	78	76
4	86	-80
5	91	-89
6	19	15
7	68	68
8	41	44
9	7	-9
10	32	-37
H=2, L=2		
0	4	-5
1	112	131
2	56	55
3	73	-76
4	93	-98
5	7	6
6	62	66
7	37	40
8	8	-3
9	33	-37
10	12	-21
H=3, L=2		
0	119	126
1	36	38
2	83	-86
3	50	-61
4	22	-21
5	41	48
6	46	49
7	8	6
8	28	-36
9	20	-26
H=4, L=2		
0	39	40
1	53	-52
2	83	-92
3	24	-30
4	24	27
5	56	61
6	8	10
7	37	-45
8	27	-34
H 5, L=2		
0	12	-14
1	68	-74
2	42	-51
3	14	20
4	53	63
5	8	10
6	34	-41
7	27	-40
H 6, L=2		
0	60	-65
1	57	-61
2	8	18
3	52	63
4	13	18
5	45	-55
6	21	-33
H=7, L=2		
0	43	-54
1	26	13
2	40	48
3	7	10
4	32	-43
5	21	-40
H 8, L=2		
0	24	25
1	60	72
2	6	11
3	25	-35
H 9, L=2		
0	39	52
1	16	25
H 1, L=2		
-1	43	-49
-2	23	22
-3	92	92
-4	56	48
-5	48	-46
-6	82	-79
-7	7	-12
-8	83	83
-9	76	86
-10	8	-12
-11	57	-58
-12	19	-20
-13	15	23
H=2, L=2		
-1	126	-149
-2	98	-111
-3	74	72
-4	142	137
-5	37	31
-6	48	-48
-7	61	-60
-8	7	4
-9	67	66
-10	50	48
-11	21	-23
-12	37	-47
-13	25	-27
H=3, L=2		
-1	5	-3
-2	119	-134
-3	90	-99
-4	93	87
-5	122	122
-6	30	24
-7	56	-62
-8	61	-58
-9	8	8
-10	57	60
-11	30	31
-12	22	-23
-13	44	-52
H=4, L=2		
-1	112	115
-2	29	24
-3	102	-109
-4	82	-85
-5	78	69
-6	111	123
-7	37	35
-8	62	-66
-9	61	-58
-10	8	2
-11	45	52
-12	22	25
-13	30	-26
H=5, L=2		
-1	74	73
-2	74	77
-3	15	9
-4	92	-92
-5	62	-53
-6	76	66
-7	101	94
-8	13	13
-9	71	-71
-10	68	-66
-11	8	18
-12	40	44
-13	18	22
H=6, L=2		
-1	7	3
-2	59	68
-3	65	69
-4	7	-11
-5	88	-76
-6	51	-41
-7	64	57
-8	74	74
-9	8	4
-10	65	-64
-11	41	-37
-12	7	10
-13	39	39
H 7, L 2		
-1	52	-54
-2	14	17
-3	68	76
-4	55	57
-5	23	-21
-6	71	-73
-7	8	-6
-8	41	35
-9	57	53
-10	25	-13
-11	65	-53
-12	41	-31
-13	20	17
H=8, L=2		
-1	36	-39
-2	42	-52
-3	15	17
-4	61	71
-5	41	44
-6	35	-35
-7	60	-60
-8	56	-45
-9	45	48
-10	42	40
-11	21	-18
-12	53	-44
-13	19	-20
H 9, L 2		
-1	12	19
-2	38	-40
-3	43	-45
-4	8	8
-5	62	55
-6	24	25
-7	41	-40
-8	82	-67
-9	18	-12
-10	43	43
-11	41	34
-12	5	-7
H=10, L=2		
-1	30	41
-2	6	7
-3	35	-42
-4	37	-45
-5	21	17
-6	50	42
-7	12	16
-8	30	-31
-9	54	-48
-10	6	-3
-11	35	37
H=11, L=2		
-4	30	-42
-5	24	-27
-6	15	12
-7	36	36
-8	5	7
-9	23	-25
H= -1, L=2		
1	55	-45
2	57	-57
3	40	36
4	153	143
5	76	67
6	62	-59
7	87	-81
8	8	7
9	60	61
10	23	23
11	38	-35
H= -2, L=2		
1	69	-56
2	75	-68
3	36	-28
4	70	62
5	88	89
6	33	28
7	68	-64
8	87	-73
9	8	2
10	55	53
11	21	19
12	26	-27
H= -3, L=2		
1	144	144
2	55	-37
3	114	-99
4	42	-35
5	71	60
6	90	77
7	17	15
8	75	-67
9	73	-59
10	8	3
11	55	49
12	17	17
H= -4, L=2		
1	154	165
2	122	106
3	69	-49
4	142	-126
5	43	-30
6	91	69
7	66	61
8	14	-11
9	87	-69
10	66	-55
11	30	27
12	45	44
H= -5, L=2		
1	17	-9
2	119	109
3	119	90
4	75	-57
5	133	-116
6	57	-39
7	87	66
8	69	60
9	14	-14
10	72	-61
11	34	-27
12	31	24
13	37	41
H= -6, L=2		
1	70	-61
2	6	5
3	96	85
4	83	62
5	72	-49
6	115	-102
7	8	2
8	50	43
9	66	52
10	8	-12
11	68	-48
12	32	-24
13	30	25
H= -7, L=2		
1	68	-53
2	68	-61
3	7	9
4	85	72
5	53	40
6	69	-57
7	92	-68
8	45	-34
9	71	58
10	53	42
11	18	-13
12	45	-37
13	14	-18
H- -8, L=2		
1	8	-5
2	91	-68
3	71	-57
4	20	8
5	75	62
6	25	22
7	70	-56
8	74	-64
9	14	8
10	71	55
11	45	29
12	5	-6
H= -9, L=2		
1	60	50
2	8	-13
3	85	-67
4	66	-56
5	42	30
6	72	59
7	25	19
8	51	-41
9	67	47
10	29	17
11	67	47
12	36	30
H= -10, L=2		
1	35	31
2	53	37
3	8	-12
4	68	-60
5	42	-28
6	32	23
7	66	54
8	17	14
9	46	-34
11	19	16
H= -11, L=2		
1	11	16
2	38	34
3	39	32
4	6	-12
5	59	-44
6	32	-20
7	37	27
8	54	44
9	26	19
10	36	-34
H= 0, L=2		
-2	47	41
-3	56	52
-4	53	-43
-5	122	-119
-6	55	-52
-7	61	65
-8	74	90
-9	8	4
-10	40	-55
-11	21	-22
-12	23	28
H= -1, L=2		
-1	57	54
-2	94	100
-3	21	-18
-4	132	-168
-5	75	-71
-6	77	79
-7	69	78
-8	8	-10
-9	54	-64
-10	23	-23
-11	23	29
H -2, L=2		
0	113	112
-1	127	132
-2	50	-41
-3	103	-128
-4	83	-85
-5	77	80
-6	67	74
-7	14	-18
-8	55	-61
-9	24	-28
-10	20	23
-11	27	40
H= -3, L=2		
0	144	152
-1	25	-24
-2	155	-170
-3	55	-51
-4	72	71
-5	65	75
-6	14	-16
-7	57	-64
-8	41	-41
-9	7	8
-10	30	41
H= -4, L=2		
0	13	-6
-1	126	-119
-2	44	-37
-3	58	56
-4	74	71
-5	8	-2
-6	35	-38
-7	43	-54
-8	7	-3
-9	29	36
H= -5, L=2		
0	95	-86
-1	52	-43
-2	37	38
-3	66	67
-4	33	34
-5	42	-48
-6	42	-49
-7	7	-13
-8	31	40
H= -6, L=2		
0	60	-47
-1	38	40
-2	52	48
-3	45	42
-4	26	-28
-5	70	-64
-6	7	-12
-7	31	40
H= -7, L=2		
0	8	10
-1	95	92
-2	58	47
-3	25	-25
-4	66	-61
-5	8	-7
-6	29	41
H= -8, L=2		
0	73	65
-1	60	54
-2	24	-19
-3	54	-50
-4	6	-9
-5	31	45
H= -9, L=2		
0	48	45
-1	30	-23
-2	48	-47
-3	5	-8
H- -10, L=2		
0	19	-17
-1	32	-43
-2	3	-12
H=0, L=3		
1	83	79
2	91	96
3	13	8
4	67	-66
5	62	-66
6	18	13
7	61	67
8	52	50
9	31	-29
10	40	-46
H=1, L=3		
0	26	23
1	106	116
2	37	33

Table II. Observed and calculated structure factors on an absolute scale.

k	Fo	Fc
3	71	-73
4	79	-87
5	7	-2
6	70	75
7	43	46
8	7	4
9	53	-57
10	4	-9
H=2, L=3		
0	92	103
1	27	29
2	70	-81
3	87	-96
4	29	-24
5	63	63
6	54	58
7	28	-29
8	28	-38
9	5	-13
H=3, L=3		
0	46	50
1	60	-62
2	80	-93
3	22	-22
4	38	45
5	42	48
6	13	-19
7	47	-51
8	13	-17
H=4, L=3		
0	45	-45
1	71	-82
2	22	-20
3	42	51
4	40	47
5	8	-16
6	47	-58
7	16	-24
H=5, L=3		
0	58	-65
1	30	-32
2	38	45
3	44	56
4	7	-3
5	43	-54
6	24	-33
H=6, L=3		
0	37	-36
1	40	47
2	53	68
3	7	7
4	32	-45
5	25	-35
H=7, L=3		
0	39	39
1	41	57
2	12	15
3	28	-37
4	16	-29
H=8, L=3		
0	59	70
1	6	-1
2	24	-32
H=1, L=3		
-1	119	-139
-2	118	-118
-3	24	19
-4	110	108
-5	72	67
-6	28	-26
-7	60	-66
-8	51	-53
-9	66	69
-10	50	59
-11	7	-1
-12	39	-52
H=2, L=3		
-1	10	8
-2	88	-92
-3	86	-82
-4	43	37
-5	126	132
-6	54	50
-7	43	-39
-8	54	-57
-9	8	-7
-10	39	38
-11	37	42
-12	6	-5
-13	38	-48
H-3, L=3		
-1	102	121
-2	44	38
-3	75	-81
-4	93	-91
-5	86	86
-6	94	100
-7	35	31
-8	55	-58
-9	65	-62
-10	8	-6
-11	32	31
-12	25	30
-13	15	-13
H=4, L=3		
-1	49	53
-2	96	113
-3	49	51
-4	77	-86
-5	74	-76
-6	29	29
-7	95	101
-8	13	14
-9	65	-65
-10	65	-59
-11	8	3
-12	35	33
-13	20	21
H=5, L=3		
-1	17	-19
-2	73	80
-3	70	84
-4	32	26
-5	79	-85
-6	78	-75
-7	22	26
-8	81	89
-9	19	17
-10	69	-74
-11	57	-54
-12	7	11
-13	38	42
H=6 L=3		
-1	42	-56
-2	12	-6
-3	39	47
-4	60	65
-5	7	-6
-6	73	-76
-7	70	-66
-8	24	19
-9	66	66
-10	8	11
-11	56	-56
-12	43	-42
-13	25	18
H=7, L=3		
-1	41	-41
-2	55	-62
-3	8	-3
-4	54	59
-5	34	33
-6	40	-40
-7	49	-49
-8	41	-43
-9	23	26
-10	55	54
-11	12	14
-12	41	-39
-13	24	-31
H 8, L=3		
-1	23	29
-2	38	-44
-3	61	-64
-4	8	0
-5	56	57
-6	19	25
-7	19	-16
-8	56	-52
-9	22	-17
-10	28	26
-11	47	44
-12	5	10
H=9, L=3		
-1	32	42
-2	26	26
-3	31	-37
-4	56	-64
-5	7	4
-6	61	56
-7	31	29
-8	36	-35
-9	45	-46
-10	6	-6
-11	35	33
-12	29	30
H=10, L=3		
-2	4	35
-3	15	19
-4	30	-43
-5	41	-48
-6	6	2
-7	47	49
-8	25	27
-9	28	-30
-10	32	-38
H= -1, L=3		
1	87	-85
2	68	63
3	95	97
4	27	21
5	92	-94
6	36	-41
7	31	28
8	55	53
9	33	31
10	20	-21
11	32	-38
H= -2, L=3		
1	143	-140
2	79	-64
3	90	77
4	126	125
5	19	-10
6	60	-61
7	38	-36
8	44	37
9	52	51
10	12	15
11	23	-26
H= -3, L=3		
1	21	-17
2	144	-130
3	68	-51
4	101	87
5	142	130
6	7	6
7	90	-84
8	43	-42
9	33	31
10	55	49
11	6	3
12	26	-28
H= -4, L=3		
1	73	69
2	61	-49
3	73	-62
4	59	-41
5	89	85
6	104	98
7	7	-2
8	88	-88
9	51	-43
10	41	39
11	48	44
12	5	-3
H= -5, L=3		
1	110	102
2	53	46
3	18	-16
4	77	-66
5	32	-19
6	94	77
7	78	63
8	14	-9
9	84	-78
10	54	-41
11	35	32
12	36	40
H= -6, L=3		
1	61	55
2	103	106
3	35	33
4	59	-50
5	73	-59
6	7	5
7	24	22
8	53	43
9	25	-20
10	77	-60
11	43	-30
12	34	28
H= -7, L=3		
1	65	-51
2	55	47
3	105	88
4	23	20
5	86	-73
6	74	-65
7	14	-6
8	58	44
9	41	30
10	12	-16
11	57	-44
12	18	-15
H= -8, L=3		
1	70	-55
2	67	-54
3	39	26
4	106	90
5	8	8
6	91	-74
7	62	-53
8	23	15
9	64	49
10	21	21
11	23	-20
12	27	-27
H= -9, L=3		
1	8	-4
2	66	-48
3	59	-49
4	42	34
5	73	62
6	8	6
7	72	-64
8	68	-49
9	29	22
10	55	49
11	20	15
H= -10, L=3		
1	32	30
2	7	-10
3	52	-42
4	39	-33
5	22	18
6	65	46
7	12	8
8	56	-47
9	41	-34
10	24	19
H= -11, L=3		
1	41	43
2	15	17
3	17	-17
4	51	-42
5	17	-18
6	29	21
7	49	40
8	8	5
9	37	-34
H=0, L=3		
-2	27	-23
-3	101	94
-4	106	97
-5	19	-18
-6	84	-88
-7	20	-18
-8	30	30
-9	69	82
-10	8	-3
-11	45	-56
-12	25	-32
H= -1, L=3		
-1	3	-35
-2	88	88
-3	97	86
-4	13	-4
-5	91	-97
-6	44	-46
-7	70	71
-8	68	81
-9	8	5
-10	38	-50
-11	22	-27
-12	3	11
H= -2, L=3		
0	43	-37
-1	78	78
-2	74	66
-3	44	-37
-4	103	-100
-5	55	-55
-6	61	59
-7	67	74
-8	20	16
-9	38	-46
-10	28	-31
-11	17	19
H= -3, L=3		
0	86	82
-1	104	93
-2	34	-24
-3	107	-111
-4	72	-77
-5	36	37
-6	64	78
-7	24	22
-8	40	-41
-9	34	-36
-10	5	5
H= -4, L=3		
0	80	86
-1	5	5
-2	91	-93
-3	86	-84
-4	12	12
-5	65	70
-6	24	17
-7	31	-34
-8	38	-42
-9	5	2
H= -5, L=3		
0	51	43
-1	76	-70
-2	96	-92
-3	7	6
-4	63	63
-5	31	24
-6	42	-46
-7	52	-52
-8	5	-6
-9	3	32
H= -6, L=3		
0	79	-71
-1	59	-47
-2	8	12
-3	74	72
-4	34	27
-5	47	-40
-6	50	-52
-7	5	-11
-8	2	27
H= -7, L=3		
0	106	-90
-1	38	34
-2	74	68
-3	43	38
-4	29	-27
-5	44	-47
-6	5	-15
H= -8, L=3		
0	8	7
-1	65	58
-2	38	37
-3	20	-13
-4	41	-43
-5	12	-18
H= -9, L=3		
0	54	46
-1	37	37
-2	6	-2
-3	25	-31
H= -10, L=3		
0	31	34
-1	5	3
H=0, L=4		
1	40	46
2	30	-25
3	77	-81
4	66	-71
5	8	6
6	46	55
7	34	31
8	24	-29
9	39	-45
10	4	4
H=1, L=4		
0	123	142
1	21	-8
2	52	-57
3	74	-78
4	22	-16
5	59	59
6	44	42
7	25	-33
8	47	-56
9	9	-12
H=2, L=4		
0	69	70
1	32	-41
2	72	-82
3	22	-17
4	67	72
5	44	46
6	33	-38
7	46	-53
8	6	-9
H=3, L=4		
0	36	-42
1	80	-87
2	8	-10
3	56	65
4	47	55
5	35	-37
6	51	-59
7	6	-10
8	2	27
H=4, L=4		
0	69	-83
1	8	-3
2	71	88
3	27	39
4	26	-26
5	40	-55
6	6	-13
H=5, L=4		
0	8	-3
1	57	71
2	44	53
3	14	-16
4	31	-41
5	15	-21
H=6, L=4		
0	43	52
1	36	50
2	8	-4
3	27	-33
4	21	-27
H=7, L=4		
0	33	46
1	7	7
2	15	-23
3	18	-26
H=8, L=4		
0	6	11
1	25	-39
H=1, L=4		
-1	52	56
-2	13	-13
-3	96	-104
-4	23	-19
-5	106	112
-6	90	90
-7	35	-32
-8	75	-91
-9	42	-41
-10	26	36
-11	31	39
-12	6	-4
H=2, L=4		
-1	44	57
-2	58	59
-3	37	-37
-4	87	-92
-5	6	-13
-6	78	78
-7	61	60
-8	49	-45
-9	76	-88
-10	21	-19
-11	33	41
-12	28	33
H=3, L=4		
-1	57	68
-2	73	87
-3	30	26
-4	68	-63
-5	72	-67
-6	7	-5
-7	65	67
-8	41	44
-9	43	-36
-10	69	-67
-11	8	-11
-12	34	34
-13	34	42
H=4, L=4		
-1	32	-37
-2	59	62
-3	76	88
-4	7	5
-5	64	-65
-6	69	-61
-7	8	-0
-8	55	55
-9	34	30
-10	43	-35
-11	57	-50
-12	7	-6
-13	37	39
H=5, L=4		
-1	74	-90
-2	38	-41
-3	56	60
-4	77	83
-5	7	-8
-6	79	-81
-7	71	-61
-8	8	15
-9	57	58
-10	33	34
-11	39	-38
-12	36	-41
-13	5	0
H=6, L=4		
-1	8	-12
-2	57	-67
-3	34	-39
-4	45	51
-5	55	64
-6	8	-10
-7	67	-68
-8	47	49
-9	25	26
-10	61	61
-11	18	13
-12	25	-29
-13	25	-34
H=7, L=4		
-1	33	37
-2	15	-20
-3	59	-65
-4	36	-30
-5	43	43
-6	47	55
-7	32	-23
-8	56	-57
-9	25	-32
-10	33	27
-11	47	47
-12	21	18
H=8, L=4		
-1	31	36
-2	18	23
-3	23	-30
-4	59	-60
-5	21	-21
-6	42	42
-7	34	29
-8	8	4
-9	54	-48
-10	12	-17
-11	32	28
-12	33	40
H=9, L=4		
-1	4	8
-2	28	37
-3	11	15
-4	21	-31
-5	47	-48
-6	7	-5
-7	47	43
-8	57	50
-9	18	-17
-10	31	-36
-11	4	-7
H=10, L=4		
-5	20	-29
-6	27	-36
-7	5	3
-8	34	43
-9	24	32
H= -1, L=4		
1	102	90
2	74	77
3	44	-37
4	97	-96
5	40	-40
6	39	32
7	61	61
8	26	28
9	21	-23
10	29	-34
H= -2, L=4		
1	86	-69
2	94	77
3	102	91
4	26	-21
5	84	-79
6	33	-27
7	43	39
8	61	58
9	13	16
10	26	-28
11	20	-31
H= -3, L=4		
1	148	-141
2	66	-50
3	91	82
4	102	104
5	18	-14
6	74	-81
7	30	-29
8	47	47
9	58	54
10	17	15
11	33	-39
H= -4, L=4		
1	53	-49
2	84	-79
3	39	-24
4	102	86
5	103	86
6	13	-11
7	74	-67
8	34	-24
9	45	41
10	59	49
11	9	-6
H= -5, L=4		
1	20	22
2	58	-50
3	76	-63
4	7	1
5	86	75
6	76	70
7	43	35
8	65	-59
9	24	-21
10	39	35
11	31	32
H= -6, L=4		
1	90	76
2	22	19
3	66	-51
4	69	-56
5	14	7
6	78	72
7	34	27
8	8	-10
9	69	-59
10	12	-13
11	34	32
H= -7, L=4		
1	58	48
2	98	84
3	24	19
4	69	-51
5	62	-50
6	22	18
7	77	61
8	46	43
9	52	-39
10	63	52
11	5	-4
H= -8, L=4		
1	43	-29
2	54	48
3	80	74
4	25	21
5	73	-57
6	58	-47
7	25	16
8	55	47
9	23	20
10	46	-38
11	41	-40
H= -9, L=4		
1	55	-44
2	24	-17
3	45	42
4	68	58
5	8	-9
6	58	-49
7	48	-39
8	19	12
9	46	40
10	5	13
H= -10, L=4		
1	17	-9
2	51	-43
3	17	-16
4	44	35
5	53	39
6	7	-8
7	57	-46
8	33	-26
9	5	9
H= -11, L=4		
2	31	-22
3	43	-40
4	5	-13
5	44	31
6	37	30
7	14	-14
8	39	-41
H=0, L=4		
-2	128	-126
-3	31	-22
-4	129	134
-5	105	99
-6	28	-27
-7	62	-63
-8	24	-24
-9	28	34
-10	35	39
-11	7	1
-12	25	-34
H= -1, L=4		
0	90	79
-1	119	-141
-2	32	-28
-3	89	92
-4	109	104
-5	27	-22
-6	61	-63
-7	19	-21
-8	26	30
-9	46	52
-10	13	13
-11	30	-34
H= -2, L=4		
0	146	-144
-1	32	-29
-2	101	104
-3	51	51
-4	6	-6
-5	61	-60
-6	34	-30
-7	26	26
-8	60	62
-9	24	28
-10	34	-34
-11	27	-42
H= -3, L=4		
0	46	-42
-1	59	53
-2	68	65
-3	11	7
-4	62	-59
-5	57	-57
-6	8	7
-7	69	76
-8	42	41
-9	22	-27
-10	34	-44
H= -4, L=4		
0	30	27
-1	74	66
-2	21	16
-3	60	-58
-4	87	-86
-5	8	11
-6	62	61
-7	42	44
-8	30	-32
-9	30	-42
H= -5, L=4		
0	86	75
-1	50	33
-2	54	-44
-3	95	-89
-4	8	-8
-5	77	76
-6	32	33
-7	30	-30
-8	31	-40
H= -6, L=4		
0	55	44
-1	91	-79
-2	75	-69
-3	8	-3
-4	73	62
-5	33	31
-6	22	-27
-7	33	-37
H= -7, L=4		
0	60	-46
-1	91	-83
-2	9	-6
-3	56	49
-4	32	30
-5	26	-27
-6	27	-37
H= -8, L=4		
0	64	-58
-1	8	-2
-2	50	41
-3	30	30
-4	6	-9
-5	28	-42
H= -9, L=4		
0	13	-11
-1	35	37
-2	37	34
-3	5	-3
H= -10, L=4		
0	31	32
-1	34	39
H=0, L=5		
1	6	-5
2	78	-77
3	60	-55
4	24	22
5	68	71
6	9	8
7	43	-48
8	29	-34
9	10	11
H=1, L=5		
0	17	15
1	81	-87
2	62	-61
3	32	27
4	62	63
5	9	15
6	43	-46
7	37	-41
8	13	-12
H=2, L=5		
0	47	-51
1	56	-57
2	19	22
3	61	67
4	33	31
5	34	-35
6	42	-53
7	6	-2
H=3, L=5		
0	62	-62
1	24	17
2	62	76
3	35	40
4	21	-20
5	41	47
6	15	-15
H=4, L=5		
0	14	8
1	59	69
2	35	43
3	20	-21
4	31	-39
5	6	-12
H-5, L=5		
0	49	62
1	36	45
2	8	-16
3	31	-41
4	10	-13
H=6, L=5		
0	33	35
1	7	-12
2	31	-39
3	12	-17
H=7, L=5		
0	7	-4
1	23	-37
H=8, L=5		
0	3	-39
H=1, L=5		
-1	84	101
-2	73	77
-3	27	-28
-4	90	-94
-5	36	-29
-6	64	68
-7	54	57
-8	8	4
-9	74	-84
-10	20	-25
-11	22	27
-12	26	36
H=2, L=5		
-1	54	47
-2	74	84
-3	45	47
-4	35	-37
-5	80	-86
-6	37	-30
-7	51	55
-8	62	66
-9	40	-37
-10	60	-65
-11	22	-23
-12	27	33
H=3, L=5		
-1	40	-48
-2	35	30
-3	63	69
-4	29	29
-5	69	-69
-6	67	-68
-7	24	-23
-8	43	43
-9	44	49
-10	15	-15
-11	43	-51
-12	6	-19
H=4, L=5		
-1	63	-72
-2	44	-53
-3	32	27
-4	66	70
-5	23	-10
-6	54	-47
-7	58	-56
-8	9	1
-9	45	45
-10	44	40
-11	8	-9
-12	34	-40
H=5, L=5		
-1	9	1
-2	68	-84
-3	58	-61
-4	31	36
-5	68	69
-6	8	4
-7	59	-59
-8	44	-41
-9	15	11
-10	57	49
-11	35	31
-12	6	-10
H=6, L=5		
-1	37	44
-2	15	-19
-3	49	-64
-4	49	-55
-5	35	39
-6	60	67
-7	9	7
-8	59	-57
-9	34	-31
-10	40	30
-11	46	45
-12	21	17
H=7, L=5		
-1	22	30
-2	20	29
-3	8	-5
-4	54	-59
-5	36	-34
-6	43	46
-7	63	62
-8	8	9
-9	43	-50
-10	22	-27
-11	25	26
-12	27	38
H=8, L=5		
-1	5	2
-2	27	33
-3	17	25
-4	7	-14
-5	37	-39
-6	7	-13
-7	18	22
-8	51	54
-9	7	1
-10	32	-42
-11	23	-28
H=9, L=5		
-3	20	34
-4	15	21
-5	16	-19
-6	24	-32
-7	17	-16
-8	27	32
-9	26	39
H= -1, L=5		
1	82	83
2	15	-8
3	82	-80
4	72	-68
5	53	44
6	60	58
7	9	6
8	42	-46
9	25	-33
H= -2, L=5		
1	64	60
2	70	61
3	7	-15
4	71	-79
5	62	-54
6	23	23
7	64	63
8	8	9
9	36	-40
10	22	-30
H= -3, L=5		
1	14	-10
2	97	82
3	37	33
4	29	-23
5	74	-74
6	43	-33
7	35	34
8	65	61
9	7	13
10	37	-42
H= -4, L=5		
1	100	-95
2	29	16
3	65	57
4	41	37
5	41	-34
6	63	-58
7	9	-14
8	36	36
9	54	47
10	6	5
H= -5, L=5		
1	91	-81
2	96	-88
3	18	9
4	99	81
5	44	35
6	62	-53
7	28	-31
8	8	1
9	42	40
10	33	35
H= -6, L=5		
1	25	16
2	76	-66
3	78	-69
4	25	19
5	102	86
6	44	35
7	33	-26
8	49	-43
9	7	6
10	33	34
H= -7, L=5		
1	64	47
2	26	16
3	48	-40
4	77	-58
5	26	23
6	87	80
7	38	31
8	35	-43
9	53	-48
10	5	4
H= -8, L=5		
1	48	39
2	49	44
3	15	13
4	56	-47
5	46	-37
6	21	19
7	72	56
8	23	23
9	46	-41
10	42	-43
H= -9, L=5		
1	8	-1
2	54	43
3	42	38
4	8	-8
5	38	-33
6	24	-23
7	18	17
8	46	42
9	9	10
H= -10, L=5		
1	54	-49
2	6	2
3	52	43
4	47	36
5	20	-14
6	35	-35
7	18	-20
8	14	16
H=0, L=5		
-1	65	71
-2	28	-23
-3	82	-87
-4	43	-40
-5	73	72
-6	79	74
-7	33	-30
-8	48	-58
-9	37	-36
-10	19	21
-11	27	34
H= -1, L=5		
-2	79	-77
-3	32	-27
-4	60	60
-5	82	81
-6	8	-4
-7	48	-61
-8	47	-45
-9	21	16
-10	35	36
-11	5	9
H= -2, L=5		
0	24	-18
-1	83	-88
-2	40	-34
-3	72	68
-4	87	91
-5	19	14
-6	56	-59
-7	44	-43
-8	15	10
-9	41	45
-10	19	23
H= -3, L=5		
0	89	-88
-1	73	-69
-2	48	45
-3	88	93
-4	38	33
-5	46	-51
-6	45	-47
-7	9	3
-8	46	51
-9	21	27
-10	13	-22
H= -4, L=5		
0	82	-80
-1	38	34
-2	94	90
-3	40	31
-4	46	-44
-5	58	-51
-6	15	14
-7	56	52
-8	29	34
-9	14	-17
H= -5, L=5		
0	30	21
-1	70	55
-2	35	28
-3	57	-46
-4	61	-50
-5	15	3
-6	55	51
-7	36	39
H= -6, L=5		
0	89	78
-1	8	-3
-2	56	-41
-3	66	-61
-4	9	-10
-5	43	42
-6	34	38
-7	5	-8
H= -7, L=5		
0	47	41
-1	41	-33
-2	63	-56
-3	24	-24
-4	38	34
-5	34	38
H= -8, L=5		
0	21	-16
-1	59	-51
-2	38	-29
-3	28	26
-4	39	43
H= -9, L=5		
0	55	-48
-1	34	-27
-2	27	27

Table II. (Contd).

CHAPTER III

STRUCTURE

III.1. Description of the Structure

Interatomic distances and bond angles were calculated by means of the function and error program ORFFE of Busing, Martin and Levy. Bond lengths and angles in the $TlCl_3$(phen) molecule are shown in Figs. 1 and 2 and listed in table III with their standard deviations. The figures show the numbering scheme which was adopted.

The phenanthroline molecule itself was found to be nearly planar; the best least squares plane passing through the ligand and the thallium atom is given by the equation:-

$$0.1864X + 0.0956Y + 0.9778Z = 1.7356$$

and the deviations from this plane are given in table IV. The three chlorine atoms were excluded from the calculation of the best plane.

TABLE IV Atomic distances (Å) from the least squares plane

Tl	0.03	Cl(1)	2.43	Cl(2)	- 0.41
Cl(3)	- 0.94	N(1)	0.00	N(2)	0.07
C(1)	0.05	C(2)	0.00	C(3)	- 0.02
C(4)	0.04	C(5)	0.01	C(6)	0.05
C(7)	0.02	C(8)	0.02	C(9)	0.04
C(10)	- 0.02	C(11)	- 0.03	C(12)	0.00

The maximum deviation from this plane is 0.07 Å and is not large enough to be statistically significant ($\Delta < 3\sigma$)

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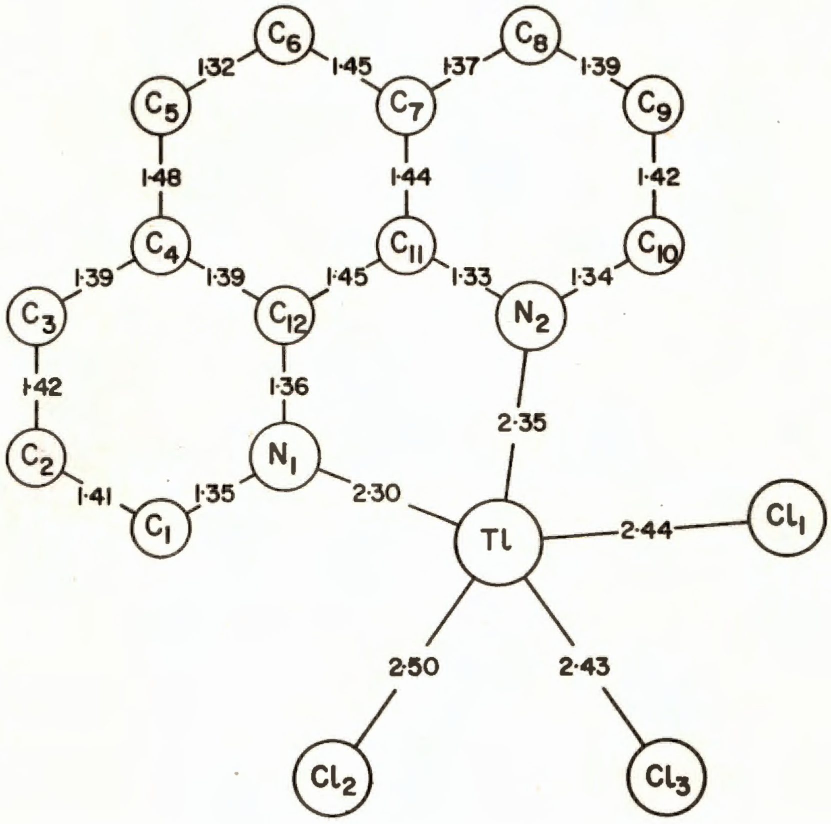

Fig. 1. Bond lengths (Å).

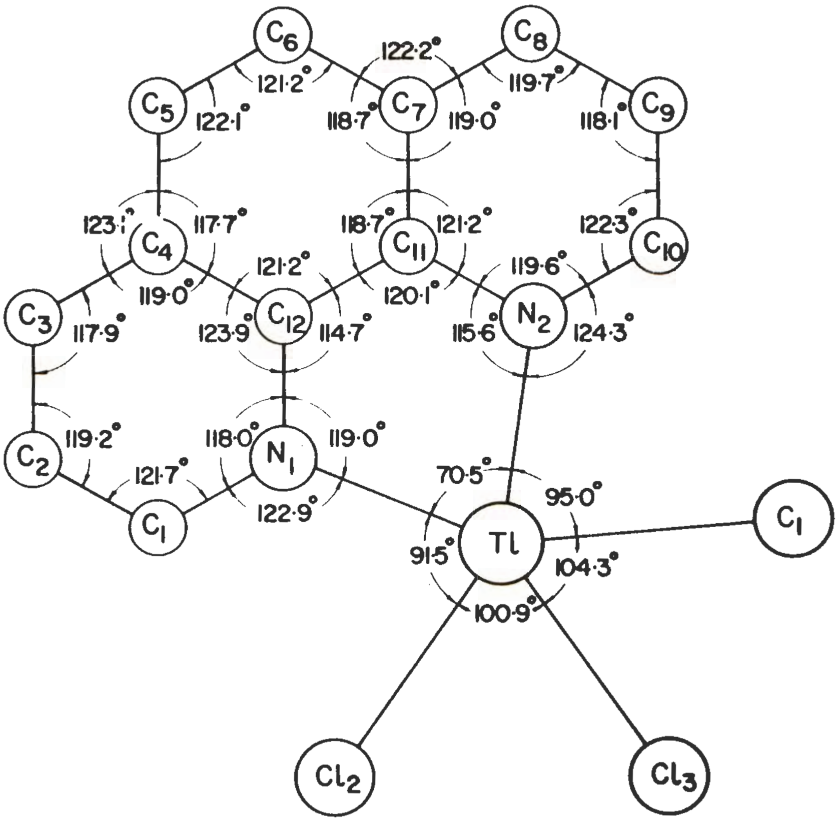

Fig. 2. Bond angles.

TABLE III Bond lengths, angles and their standard deviations

	Å		Å
C(1) - C(2)	1.41 ± 0.05	Tl - N(2)	2.35 ± 0.02
C(2) - C(3)	1.42 ± 0.05	Tl - N(1)	2.30 ± 0.03
C(3) - C(4)	1.39 ± 0.05	Average	2.33 ± 0.03
C(4) - C(5)	1.48 ± 0.05		
C(5) - C(6)	1.32 ± 0.05	Tl ... C(1)	3.24 ± 0.04
C(6) - C(7)	1.45 ± 0.05		
C(7) - C(8)	1.37 ± 0.05		
C(8) - C(9)	1.39 ± 0.05	Cl(1)...Cl(2)	3.79 ± 0.04
C(9) - C(10)	1.42 ± 0.05	Cl(1)...Cl(3)	3.84 ± 0.02
C(11) - C(12)	1.45 ± 0.04	Cl(2)...Cl(3)	3.80 ± 0.03
C(7) - C(11)	1.44 ± 0.04		
C(4) - C(12)	1.39 ± 0.04	Cl(1)...N(1)	3.64 ± 0.04
Average C-C	1.41 ± 0.05	Cl(1)...N(2)	3.53 ± 0.03
		Cl(2)...N(1)	3.44 ± 0.03
N(1) - C(1)	1.35 ± 0.04	Cl(2)...N(2)	4.76 ± 0.03
N(1) - C(12)	1.36 ± 0.04	Cl(3)...N(1)	4.57 ± 0.04
N(2) - C(10)	1.34 ± 0.04	Cl(3)...N(2)	3.38 ± 0.03
N(2) - C(11)	1.33 ± 0.04		
Average C-N	1.34 ± 0.04		
		Cl(2)...C(1)	3.41 ± 0.03
N(1)...N(2)	2.68 ± 0.04		
		Cl(3)...C(10)	3.47 ± 0.04
Tl - Cl(1)	2.44 ± 0.02		
Tl - Cl(2)	2.50 ± 0.01		
Tl - Cl(3)	2.43 ± 0.02		
Average Tl-Cl	2.46 ± 0.02		

N(1) - C(1) - C(2)	121.7 ± 2.9°
C(1) - C(2) - C(3)	119.2 ± 3.3
C(2) - C(3) - C(4)	117.9 ± 3.2
C(3) - C(4) - C(12)	119.0 ± 3.0
C(4) - C(12) - N(1)	123.9 ± 2.9
C(12) - C(4) - C(5)	117.7 ± 3.0
C(4) - C(5) - C(6)	122.1 ± 3.1
C(5) - C(6) - C(7)	121.2 ± 2.8
C(6) - C(7) - C(11)	118.7 ± 2.7
C(7) - C(11) - C(12)	118.7 ± 2.6
C(11) - C(12) - C(4)	121.2 ± 2.7
C(11) - C(7) - C(8)	119.0 ± 2.7
C(7) - C(8) - C(9)	119.7 ± 3.0
C(8) - C(9) - C(10)	118.1 ± 3.3
C(10) - N(2) - C(11)	119.6 ± 2.5
N(2) - C(11) - C(7)	121.2 ± 2.7
Average	119.9 ± 3.0°

TABLE III Bond lengths, angles and their standard deviations cont.

Cl(2) - Tl - Cl(3)	100.9 ± 0.6°
Cl(2) - Tl - Cl(1)	100.4 ± 0.7
Cl(1) - Tl - Cl(3)	104.3 ± 0.5
Cl(3) - Tl - N(2)	89.9 ± 0.8
Cl(1) - Tl - N(2)	95.0 ± 0.9
Cl(2) - Tl - N(2)	158.2 ± 0.6
Cl(2) - Tl - N(1)	91.5 ± 0.9
Cl(3) - Tl - N(1)	149.6 ± 0.9
Cl(1) - Tl - N(1)	100.5 ± 0.9
N(1) - Tl - N(2)	70.5 ± 1.0
Tl - N(2) - C(10)	124.3 ± 2.0
C(11) - N(2) - C(10)	119.6 ± 2.5
Tl - N(2) - C(11)	115.6 ± 2.0
Tl - N(1) - C(12)	119.0 ± 2.1
C(1) - N(1) - Tl	122.9 ± 2.0
N(2) - C(11) - C(12)	120.1 ± 2.5
N(1) - C(12) - C(11)	114.7 ± 2.6
C(3) - C(4) - C(5)	123.1 ± 3.1

The mean C-C and C-N bond lengths in the ligand are 1.41 ± 0.02 Å and 1.34 ± 0.02 Å respectively. These values are in good agreement with the mean carbon-carbon distances of 1.40 ± 0.01 Å and 1.34 ± 0.01 Å for the C-N bond lengths reported for dichloro (1,10-phenanthroline)-zinc (II) by Weiland et al.(28)

The thallium atom is bonded to the bidentate ligand through the two ring-nitrogens. The two thallium-nitrogen bond lengths are 2.30 Å and 2.35 Å which are significantly shorter than the 2.57 Å reported for dimethyl 1,10-phenanthrolinethallium perchlorate(29). The angle between the two thallium-nitrogen bonds is restricted by the geometry of the phenanthroline molecule and is 70.5°. The N-Tl-N angle for the dimethyl-1,10-phenanthroline-thallium perchlorate is 63°. This difference in bond angles is caused by the shorter Tl-N bonds in the former phenanthroline complex.

The geometry of the phenanthroline molecule is similar to that of the phenanthrene molecule determined by Trotter(30). Phenanthroline differs from phenanthrene in that the former contains two nitrogen atoms which are replaced by carbon atoms in the latter. In the phenanthroline molecule the C(11) - C(12) bond is longer than the C(5) - C(6) bond while bonds C(7) - C(8) and C(3) - C(4) are longer than bonds C(10) - N(2) and C(1) - N(1) respectively. Corresponding bonds in phenanthrene show equivalent length effects.

The distances between thallium and the chlorine atoms are shorter than those hitherto reported (see table V)

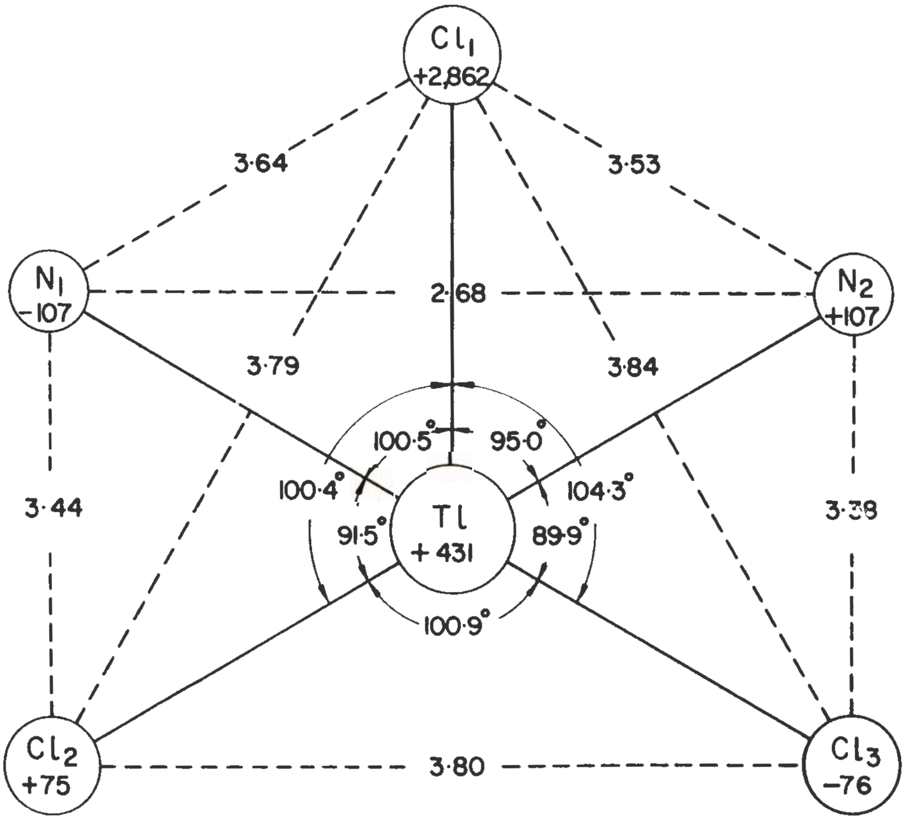

Fig. 3. Five ligand atoms around thallium(III) with bond lengths (Å) and angles. Displacement of atoms from the mean plane through Cl(2), Cl(3), N(1) and N(2) are given in the circles in units of 10^3 Å.

and are significantly shorter than the sum of their ionic radii.

TABLE V The Tl-X bond lengths in halogeno-thallium complexes

Substances	$TlCl_3(phen)$	$K_3TlCl_62H_2O$(31)	$Cs_2TlCl_5H_2O$(32)
Tl-Cl	2.46 Å	2.55	2.53

Substances	$Co(NH_3)_6TlCl_6$(33)	$r(Tl^{+3}) + r(Cl^-)$(34)
Tl-Cl	2.48	2.76

The mean plane through atoms Cl(2), Cl(3), N(1) and N(2), referred to orthogonalised axes, is

$$0.3980X + 0.0941Y + 0.9126Z = 1.3463$$

Fig. 3 shows the arrangement of the atoms which are bonded to the thallium atom with their deviations (x10^3 Å) from this plane. The complex molecule has a square-pyramidal structure; the thallium atom lies above the basal plane formed by the two chlorine and the two nitrogen atoms, and the third chlorine occupies the apical position.

It can be seen from TABLE III that the distances between non-bonded atoms in the molecule are all greater than the sum of their van der Waals radii. No distortion due to close approaches between non-bonded atoms is evident.

A perspective view of the molecule to illustrate its conformation is given in Fig. 4. A non-crystallo-

/graphic...

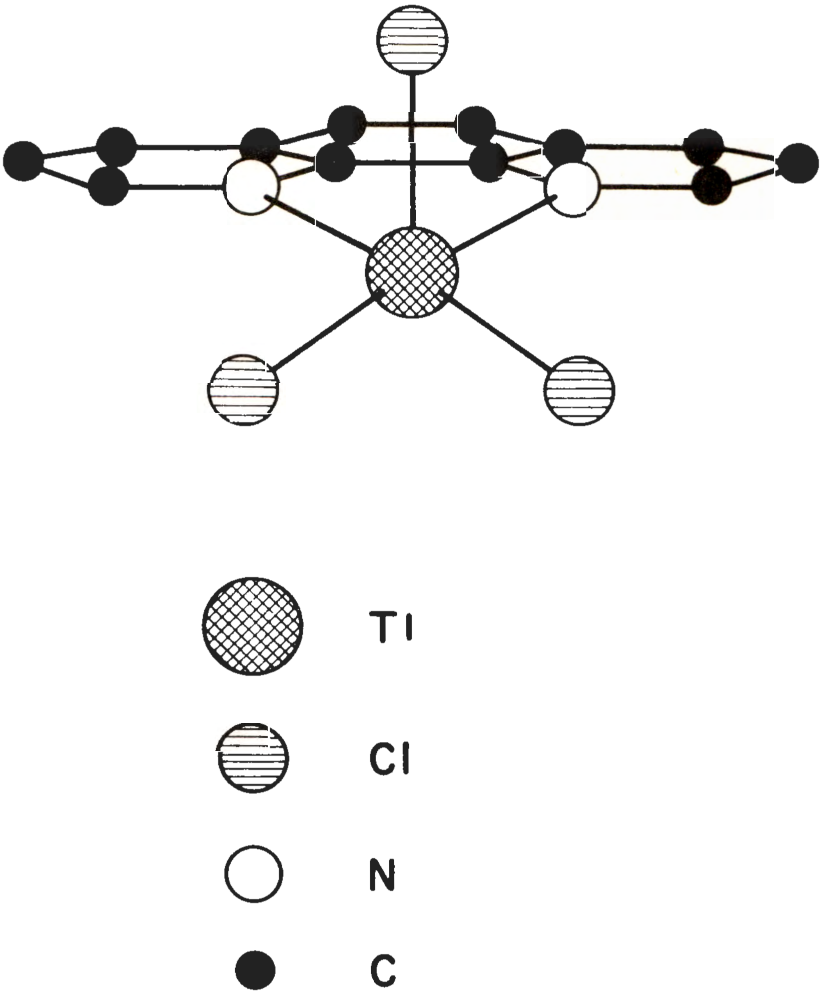

Fig. 4. Perspective view of the molecule to illustrate its conformation.

TABLE VI Intramolecular distances between two atoms related by

a) a centre of symmetry at the origin

	Å
Tl . . . Tl	4.48 ± 0.04
Tl . . . Cl(2')	3.21 ± 0.03
Cl(2) ... Cl(2')	3.62 ± 0.03
Cl(2) ... Cl(3')	3.73 ± 0.03
Cl(2) ... N(1')	3.40 ± 0.04
Cl(2) ... N(2')	3.83 ± 0.04
Cl(2) ... C(1')	3.93 ± 0.04
Cl(3) ... C(1')	3.40 ± 0.05
Cl(3) ... C(2')	3.73 ± 0.05

b) translation of one unit cell in the x-direction

	Å
C(3) . . . Cl(1)	3.89 ± 0.04
C(3) . . . Cl(3)	3.75 ± 0.04
C(4) . . . Cl(3)	3.87 ± 0.04
C(6) . . . Cl(3)	3.57 ± 0.05

c) translation of one unit cell in the y-direction

Cl(2) . . . C(8)	3.52 ± 0.04

d) translation of one unit cell in the z-direction

Cl(3) . . . Cl(1)	3.80 ± 0.02

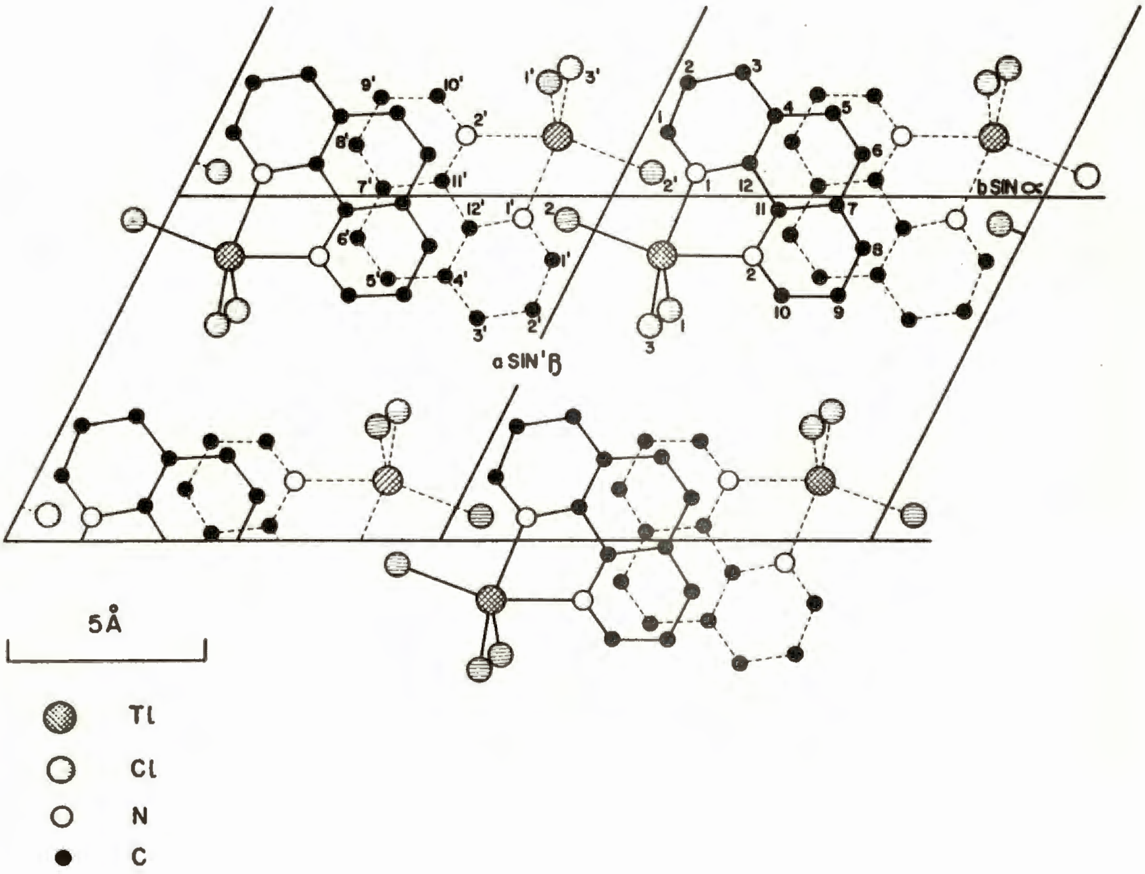

Fig. 5. Projection of the structure along c. The molecules with bonds shown in dashed lines are below the molecules drawn with solid lines and are related by a centre of symmetry at the origin.

graphic mirror plane containing the thallium and chlorine (Cl(1)) bisects the phenanthroline molecule.

All intramolecular distances are given in TABLE VI. The closest approach between molecules is between the two which are related by the centre of symmetry at the origin. The Tl...Tl distance is 4.48 ± 0.04 Å which is much larger than Tl-Tl of 3.22 Å in Na_2Tl(35). The closest approach in elemental thallium is 3.40 Å.

The Cl(2') ...Cl(2), Cl(2')...Cl(3) and Cl(2')...N(1) distances are never less than the sum of their van der Waals radii. These distances are shorter than the corresponding Cl(2)...Cl(3) and Cl(2)...N(1) distances within the molecule. The observed Tl . . .Cl(2') distance is significantly longer than 2.76 Å (34) which is the sum of the thallic ion radius and the van der Waals radius of chlorine.

The distances between two molecules related by unit cell translations in the x, y and z directions are all larger than the usual van der Waals separations mentioned in TABLE VI and thus have little bearing on the structure.

This structure thus falls into the "molecular" class in which the only interactions between molecules are of the van der Waals type. Figure 5 gives the c-axis projection of the crystal structure.

III.2. Discussion

The large standard deviations (0.05 Å in C-C bonds and 0.04 Å in C-N bonds and 3° in the bond angles) are due to the dominant scattering power of the thallium atom.

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The bond lengths and angles are as expected for the ligand. The mean C-C and C-N distances compare favourably with the C-C (1.39 ± 0.005 Å) and C-N distances (1.37 ± 0.03 Å)(36) for pyridine.

The Tl-Cl and Tl-N bond lengths are shorter than those previously reported. This suggests that the bonding is covalent with an ionic character. The equation of Hannay and Smyth gives the percentage ionic character Ic of a bond as:-

$$Ic = 16\Delta x + 3.5(\Delta x)^2$$

where Δx is the difference in electronegativity. The percentage ionic character of the Tl-Cl bond is 24.2% in this case, taking the difference in electronegativity as 1.2 (3.0 - 1.8) from Pauling. Bonds of 50% or greater ionic character are considered to be ionic by Kleinberg *et al.*(37).

The polarizability of an atom or ion measures the ease with which its electron distribution may be distorted. When a cation and an anion approach one another, the field surrounding each ion polarizes the other to an extent determined by their polarizabilities. The major effect is usually the polarization of the anion by the cation. If the polarization is extensive, the electrons are drawn towards the cation and the bond has an appreciable covalent character. The tendency of an anion to form a covalent bond with a cation i.e., to coordinate covalently with the cation, is thus markedly dependent on the polarizability. The effective nuclear charge in the chlorine ion is reduced by the addition of an extra electron and it is thus easily polarized by a cation. Factors which increase the effective field strength about the cation are; a decrease in the ionic radius, an increase in charge and an eighteen electron configuration. All these factors are present in the thallic ion and it thus has a high effective electrostatic field associated with it. The chlorine ion thus becomes strongly polarized and covalent bonding will consequently be favoured.

The close approach between Tl...Cl(2') seems significant at first glance. From the packing point of view the thallium atom thus has an octahedral environment with the one apex occupied by Cl(2'). The distance of 3.2 Å is however much larger than the normal van der Waals separation and the chlorine atom is thus not chemically bonded to the thallium atom.

All atoms surrounding the thallium atom within van der Waals distances are considered to belong to the thallium coordination sphere (after Grdenic(38)). The complex thus contains a genuine five-coordinated Tl^{+3} ion with atoms bonded to it at the corners of a square-pyramid. The structure is not ideal as the thallium atom is above the basal plane, while Cl(2) and N(2) are slightly above the plane and Cl(1) and N(1) are below it. Analogous displacements of the metal atoms from the basal planes have been reported for $Co(NO)(S_2N[C_2H_5]_2)_2$, 0.54 Å; $Co[OAsCH_3(C_6H_5)_2]_4(ClO_4)_2$, o.32 Å and VO $(acac)_2$, 0.56 Å(39).

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The solubility of $TlCl_3$(phen) in donor solvents can be understood in terms of its structure. The thallium ion can be considered to posess an octahedral environment with a vacant apex. In solution this vacant position would be occupied by a molecule of the solvent:

$$TlCl_3(\text{phen}) + \text{solvent} \rightleftharpoons [TlCl_3(\text{phen})\ \text{solvent}]$$

The complex thus becomes six-coordinated in solution. The tendency of thallic ion to attain either a tetrahedral or octahedral arrangement is evidenced by the stereochemistry of various compounds of thallium which have been reported(31 - 33). This tendency also explains the formation of the dimeric electrolyte $[TlX_2L_4][TlX_4]$ in solution during electrical conductivity experiments.

The valence bond theory is used to explain the bonding in the $TlCl_3$(phen) complex. Each of the ligands is considered as the donor of an electron pair to the metal ion. The metal ion must have a set of equivalent σ- orbitals, equal to the number of ligands, available in order to accept these electron pairs.

There are two basic configurations that can be adopted by the complex compounds of coordination number 5; the trigonal-bipyramidal and the square-pyramidal. (See page 39).

There has been speculation as to whether a $d_{x^2-y^2}$ or a d_{z^2} orbital would be hybridised with the s- and

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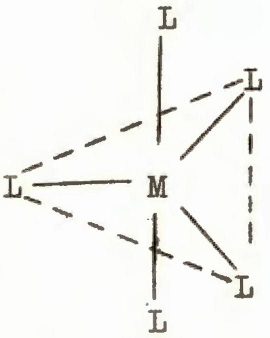
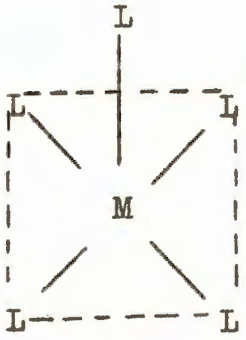
three p-orbitals in five-coordinated complexes. Daudell and Bucher(40) predicted from theory that the d_{z^2} orbital would be used in trigonal-bipyramidal bonds and the $d_{x^2-y^2}$ in square-pyramidal bonds.



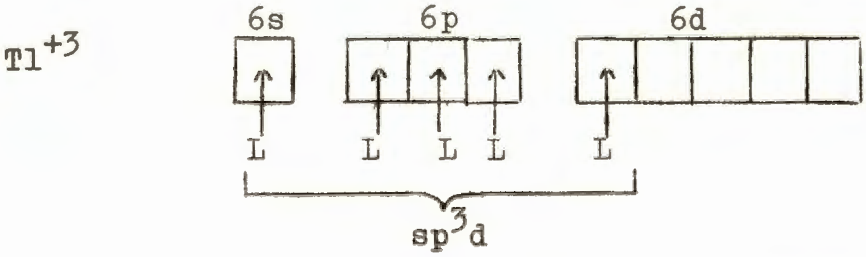
Trigonal-bipyramidal



Square-pyramidal

The trigonal-bipyramidal orbitals consists of two different sets of hybrids; sp^2 (giving the three trigonal-planar bonds) and $d_{z^2}\ p_z$ (giving the two linear axial bonds). In the same way, the square-pyramidal hybrids can be viewed as $d_{x^2-y^2}\ sp^2$ (giving four square-planar bonds) and p_z (giving the apical bond).

The thallic ion has no vacant inner d orbitals and must use a higher $d_{x^2-y^2}$ orbital. The configuration of the thallium ion in trichloro 1,10-phenanthroline-thallium (III) is therefore indicated below:



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There is a close resemblance in the physical properties of thallic chloride complexes with neutral ligands such as 1,10-phenanthroline (phen), 2,2'bipyridyl (bip) and pyridine (py). This warrants further X-ray investigation of these complexes to determine whether they have similar crystal structures. An X-ray investigation to this end is at present underway. Both the bipyridyl and phenanthroline compounds are soluble in donor solvents, their electrical conductivities in organic solvents are the same as are their solid state far infrared spectra.

Preliminary oscillation, zero and first layer line Weissenberg photographs of $TlCl_3$(bip) showed that its crystals belong to the triclinic system. It is however not isomorphous with $TlCl_3$(phen). The cell dimensions are

$a = 9.36 \pm 0.02$ Å $\alpha = 97.1 \pm 0.5^\circ$

$b = 9.86 \pm 0.03$ Å $\beta = 124.3 \pm 0.5^\circ$

$c = 9.19 \pm 0.02$ Å $\gamma = 105.3 \pm 0.3^\circ$

Cell volume = 635 $Å^3$

The density was determined using the flotation method and found to be 2.43 g cm^{-3} which agrees satisfactorily with the value of 2.44 g cm^{-3} calculated on the basis of two molecules per unit-cell.

A thermochemical investigation of the complex formation of thallium (III) in aqueous solution has been carried out by Kul'ba <u>et al</u>.(41). They found that the ligand-metal bond is more stable for 1,10-phenanthroline

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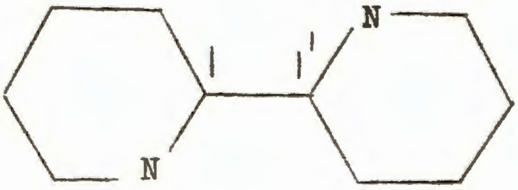
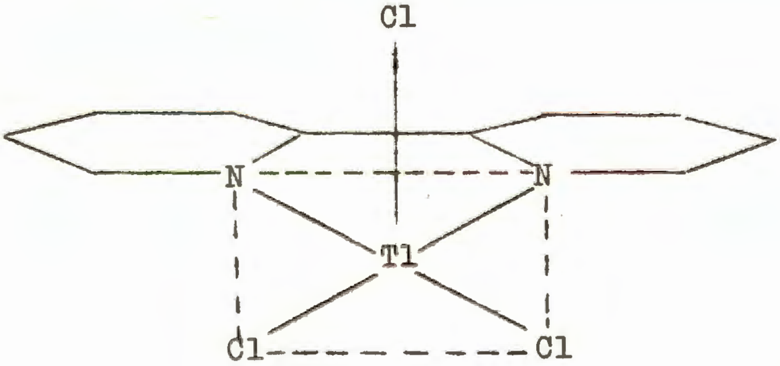
than for 2,2'-bipyridyl. An X-ray structure analysis showed that the 2,2'-bipyridyl is planar with nitrogens in the trans-position.



The length of the C(1)-C(1') bond (1.5 Å) allows rotation of the plane rings about this bond and this is apparently what occurs when coordination takes place. The resulting structure has a reduced stability because of the energy taken up in attaining the cis-configuration. This cis-configuration of 2,2'-bipyridyl is very similar to that of 1,10-phenanthroline except that it has two carbon atoms less.

All this implies that the structure of $TlCl_3$(bip) would be expected to be similar to that of $TlCl_3$(phen) and the following square-pyramidal structure is proposed for this compound.



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III.3. Conclusion

The X-ray investigation proved conclusively that $TlCl_3$(phen) is a genuine five-coordinated compound. The square-pyramidal structure explains many of its observed physical properties. The close resemblances in the physical properties of tervalent thallium halide complexes with neutral ligands warrant their further investigation to see whether they have similar crystal structures. An X-ray investigation to this end is at present underway.

ABSTRACT

The crystal structure of $TlCl_3$(phen) has been determined from an X-ray study of a single crystal. The triclinic cell, space group $P\bar{1}$, with $a = 9.44$ Å, $b = 10.94$ Å, $c = 7.55$ Å, $\alpha = 98.2^\circ$, $\beta = 96.6^\circ$ and $\gamma = 115.9^\circ$, contains two formula units. The structure was determined by standard crystallographic techniques and the atomic parameters were refined by a full-matrix least square procedures. The value of R is 13.0%.

The thallic ion has a square-pyramidal environment and the bonding between the central atom and the ligands is covalent. The structure explains many of the observed physical properties of the compound and a square-pyramidal structure is proposed for $TlCl_3$(bip).

SAMEVATTING

Die kristal- en molekulêre struktuur van $TlCl_3$(phen) is met behulp van drie-dimensionale X-straaldiffraksiemetodes bepaal. Die trikliniese sel wat behoort tot die ruimtegroep $P\bar{1}$, het die volgende eenheidselafmetings a = 9.44 Å, b = 10.94 Å, c = 7.55 Å, $\alpha = 98.2^\circ$, $\beta = 96.6^\circ$, en $\gamma = 115.9^\circ$. Volgens eksperimentele digtheid 2.39 g cm^{-3}, is daar 2 formule-eenhede per eenheidsel. Die ligand wat kovalent gebonde is aan die sentrale thallium atoom, is vierkantigpiramidaal om hierdie sentrale atoom gerangskik. Die struktuur bied 'n verklaring vir die waargenome fisiese eienskappe van die verbinding en 'n soortgelyke struktuur word voorgestel vir $TlCl_3$(bip) op grond van die sterk ooreenkoms in fisiese eienskappe.

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