THIOETHER AND RELATED LIGAND COMPLEXES OF COPPER

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A thesis presented in partial
fulfillment of the requirements
for the degree of
Master of Science.

Chemistry / Biochemistry / Biophysics Department
Massey University
October 1975

ABSTRACT

The dithioethers 2,5-dithiahexane (DTH) and 3,6-dithiaoctane (DTO) form the following stable copper (II) complexes; $Cu(S\frown S)X_2$ where $S\frown S$=DTH or DTO and X=Cl or Br, and also $Cu(DTH)_2(BF_4)_2$. The complexes $Cu(DTO)_2(BF_4)_2$ and $Cu(DTO)(NO_3)_2.H_2O$ decomposed over a short period of time. The following copper (I) complexes were also prepared: $[(CuX)_2DTO]_n$ where X=Cl or Br, Cu(DTO)I, Cu(DTH)Cl, $[Cu(DTH)X]_n$ where X=Br or I, $[Cu(DTO)SCN]_n$ and $Cu(DTO)_2BF_4$. The complexes were characterised using infra-red spectroscopy, visible-U.V. spectroscopy, Raman spectroscopy, x-ray powder photography, conductivity and molecular weight measurements, and proton nuclear magnetic resonance spectroscopy. Some reactions were also carried out by displacement of the dithioethers with a variety of monodentate and bidentate ligands, e.g. pyridine, ethylenediamine, trimethylphosphine sulphide, sodium dimethyldithiophosphinate dihydrate, and triphenylphosphine which also forms an adduct with Cu(DTH)Cl to give $Cu(DTH)(\phi_3P)Cl$.

ACKNOWLEDGEMENTS

I am very grateful to:

my supervisors, Dr E.W. Ainscough and Dr A.M. Brodie for their sincere interest and very valuable guidance in this project.

Dr M.D. Taylor of the Chemistry Department, Auckland University for the use of the interferometer for far infrared spectra.

Professor A.D. Campbell of Otago University for microanalyses and molecular weight determinations.

Dr J.H. Kirkman of the Soil Sciences Department, Massey University for the use of powder x-ray equipment.

Mr A.A. Trow of Massey University for ^{1}H. nuclear magnetic resonance spectra.

Dr G.G. Midwinter of the Chemistry, Biochemistry, Biophysics Department, Massey University for the use of Beckmann Acta spectrophotometer.

Dr G. Burns of the Chemistry Department, Victoria University for the use of the Raman spectrometry equipment.

Also my appreciation to my wife who typed this work and provided support and encouragement.

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CHAPTER 1

INTRODUCTION

Thioethers do not generally coordinate very readily to metals but their coordinating ability is enhanced by chelate ring formation.[1] The dithioethers, 2,5-dithiahexane (DTH) and 3,6-dithiaoctane (DTO), form chelate complexes with a large variety of transition metals. DTH forms both mono and bis chelate complexes with Pt(II)[1-4], Pd(II)[2,5], Hg(II)[2-5], Cd(II)[2,5], Zn(II)[6], Sn(IV)[4,6,16], Bi(III)[6], Au(I)[6], Au(III)[6], Ni(II)[3,5,7-10], Co(II)[7,8], Cu(II)[3,6,8,22], Cu(I)[5,12], Ti(IV)[16], V(IV)[16] and $W(CO)_4$[19] whilst it forms bridging complexes with Mo(II)[11], Rh(III)[4,5], Re(III)[12,13], and Cu(I) acetate[15]. DTO forms chelate complexes with Co(II)[7]. Ni(II)[9], Ti(IV)[16], V(IV)[16], Sn(IV)[16], Pt(II)[18], Cu[8,17] and both chelates and bridges in complexes of chromium carbonyls[20,21].

Very little work has been done with copper compounds containing thioether ligands generally yet these are considered to be important in biological systems. Thioethers are potential binding sites for metal ions in proteins and enzymes, due to the natural occurrence of compounds like L-methionine which is found in most proteins, and d-biotin[22]. Rheinburger and Sigel[23] commented that the interactions between simple thioethers and biologically important metal-ions like Mn^{2+}, Cu^{2+}, Zn^{2+} have hardly been investigated. This is especially noticeable for the dithioethers DTH and DTO where no complexes with Mn(II) have been reported, only one report of Zn(II)[6] complexes but no characterisation, and again the preparation of a very limited number of Cu(I)[5,12] and Cu(II)[3,6,8,17,22] complexes but no characterisation. The complexes previously prepared are $Cu(DTH)Cl_2$ [8,14,22], Cu(DTH)Cl [14], Cu(DTH)Br [14], $Cu(DTO)Cl_2$ [17], $Cu(DTH)_2(BF_4)_2$ [8,22], $Cu(DTH)_2(ClO_4)_2$ [8,22] and $(CuOOCCH_3)_2DTH$ [15].

A recent development is the discovery of Cu(II) and Fe(III) complexes of N-methylthioformylhydroxamic acid in the culture broth of Pseudomonas fluorescens [24]. It was simultaneously reported that the same ligand could be secured by the removal of copper from the antibiotic YC73 which is produced by a 'pseudomonad' culture [24]. This is indicative that copper complexes of sulphur containing ligands may be important as antibiotics.

Much investigation has been done on 'blue' copper proteins which are thought to contain sulphur and nitrogen donors. Spiro et al [25] have investigated this using a tunable dye laser to give resonance enhanced Raman spectra for azurin, ceruloplasmin, and plastocyanin. These proteins are important enzymes in electron transfer processes. From their spectra they assigned a weak band near $270 cm^{-1}$ to be a (Cu-S) stretching frequency.

Further evidence of copper sulphur bonding in proteins is from x-ray photoelectron spectroscopy [26] of bean plastocyanin where a shift of the S2p binding energy was observed on coordinating the apo-protein with Cu(II) and Cobalt(II).

It is also generally known that sulphur compounds readily reduce copper(II) to copper(I)[1]. This is especially true for thiols, and dithiophosphinates and to a lesser extent xanthates and dithiocarbamates.

In this project copper complexes of DTO and DTH have been synthesised and characterised by a variety of physical techniques, in order to gain further information about copper(I) and copper(II) atoms in a sulphur ligand environment. Reactions using a variety of monodentate and bidentate ligands with some complexes were carried out.

CHAPTER 2

COPPER(II) COMPLEXES

2.1 Syntheses

The following copper(II) complexes were prepared: $Cu(DTH)X_2$ where X=Cl or Br; $Cu(DTO)X_2$ where X=Cl or Br; $Cu(DTO)_2(BF_4)_2$; and $Cu(DTO)(NO_3)_2.H_2O$.

Of the copper(II) complexes of 3,6-dithiaoctane (DTO) only the chloro complex was easily isolated by direct precipitation from acetone. The bromo complex was prepared by a method similar to that used by Carlin and Weissburger [7] in their preparations of cobalt(II) halide complexes with 2,5-dithiahexane and 3,6-dithiaoctane, i.e. the addition of neat DTO to solid $CuBr_2$(anhydrous).

The nitrato complex appeared to be very hygroscopic and could only be isolated in a pure form from strong dehydrating solvents such as 2,2-dimethoxypropane (DMP) and triethyl-orthoformate (TEOF). Similarly for the copper(II) tetra-fluoroborate complex which was isolated from TEOF as a brown precipitate.

Once isolated as solids the bromo and chloro complexes appeared to be stable under atmospheric conditions but the nitrato and tetrafluoroborate decomposed after a short period of time (2-3 weeks) in a dessicator.

The chloro and bromo copper(II) complexes of DTH were both easily isolated from solution; the chloro complex from acetone and the bromo complex from ethanol. The chloro complex has previously been prepared [8,14,22], also $Cu(DTH)_2X_2$ where X=BF_4 or ClO_4 [8,22] and $Cu(DTH)_2BF_4$ [22]. The tetra-fluoroborate and perchlorate complexes were not reattempted.

For detailed methods of preparation and analytical results see chapter 2.4.

2.2 Infra-red Spectra

The crystal structure of bis(2,5-dithiahexane)copper(II)-tetrafluoroborate has been determined in this laboratory by Norris.[27] This structure shows that the DTH ligand is chelated (see figure 2.2a). The infra-red spectra in the range 1600 cm^{-1} to 600 cm^{-1} for the complexes Cu(DTH)X_2 where X=Cl or Br show the same pattern of ligand bands as Cu(DTH)$_2$(BF$_4$)$_2$, indicating that the DTH ligand is chelating in all the copper(II) complexes. The copper(II) DTO complexes all have similar infra-red spectra to the Cu(DTO)$_2$(BF$_4$) complex which has a chelating DTO ligand (see chapter 3.11 for discussion) indicating that in all the copper(II) DTO complexes the ligand is also chelating. See figure 2.2b for comparison of spectra. There is a strongly tetragonolly distorted environment around the copper atom in Cu(DTH)$_2$(BF$_4$)$_2$ with a plane of four sulphur atoms around the copper and a fluorine atom from each of the BF$_4$ groups weakly coordinated in the axial positions. The infra-red spectrum of this complex shows bands due to the BF$_4$ at 1050 cm^{-1} and 970 cm^{-1} that are very broad, and also a band at 510 cm^{-1}. A sharp medium intensity band also occurs at 760 cm^{-1}. Nakamoto[28] reports the spectra of ionic BF$_4$ as ν_1 =769 cm^{-1}; ν_2=353 cm^{-1}; ν_3 =984 cm^{-1}; and ν_4=524 cm^{-1}. All these bands are Raman active but only ν_3 and ν_4 are infra-red active. Bew et al[29] found

Figure 2.2a Perspective View of $Cu(DTH)_2(BF_4)_2$ [27]

Where DTH=2,5-dithiahexane.

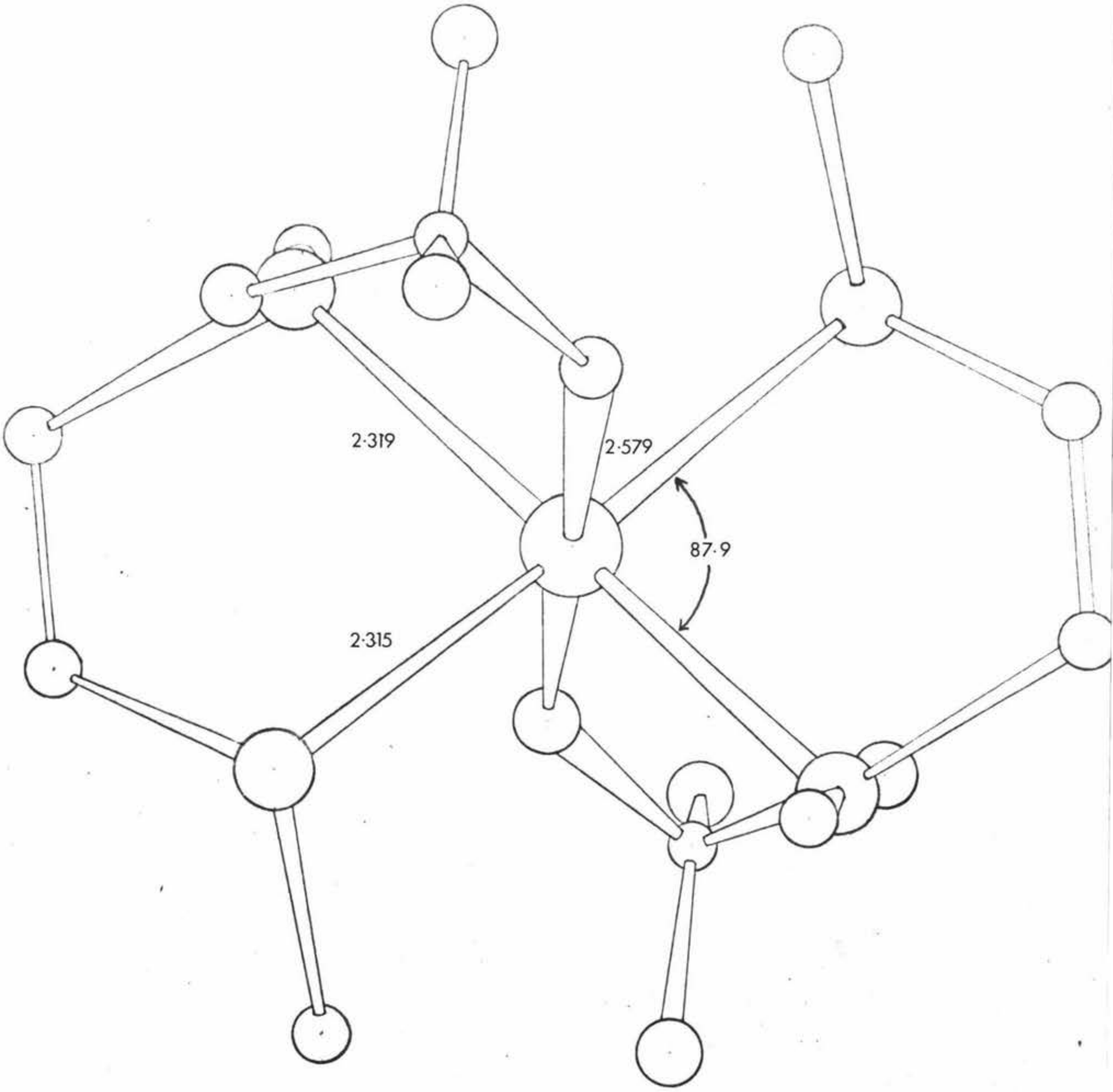
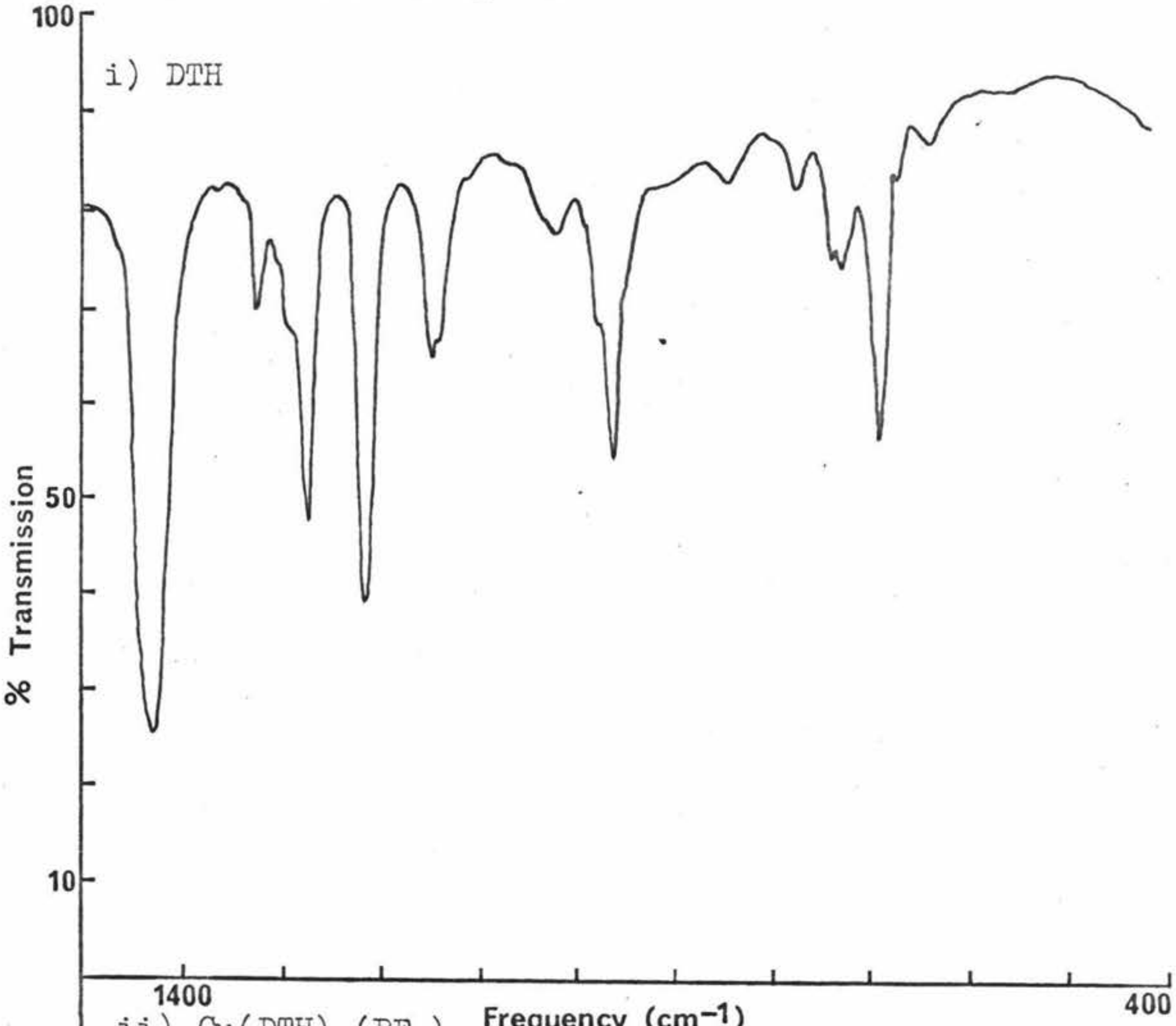


Figure 2.2b Infra-red Spectra



i) DTH

ii) Cu$(DTH)_2(BF_4)_2$

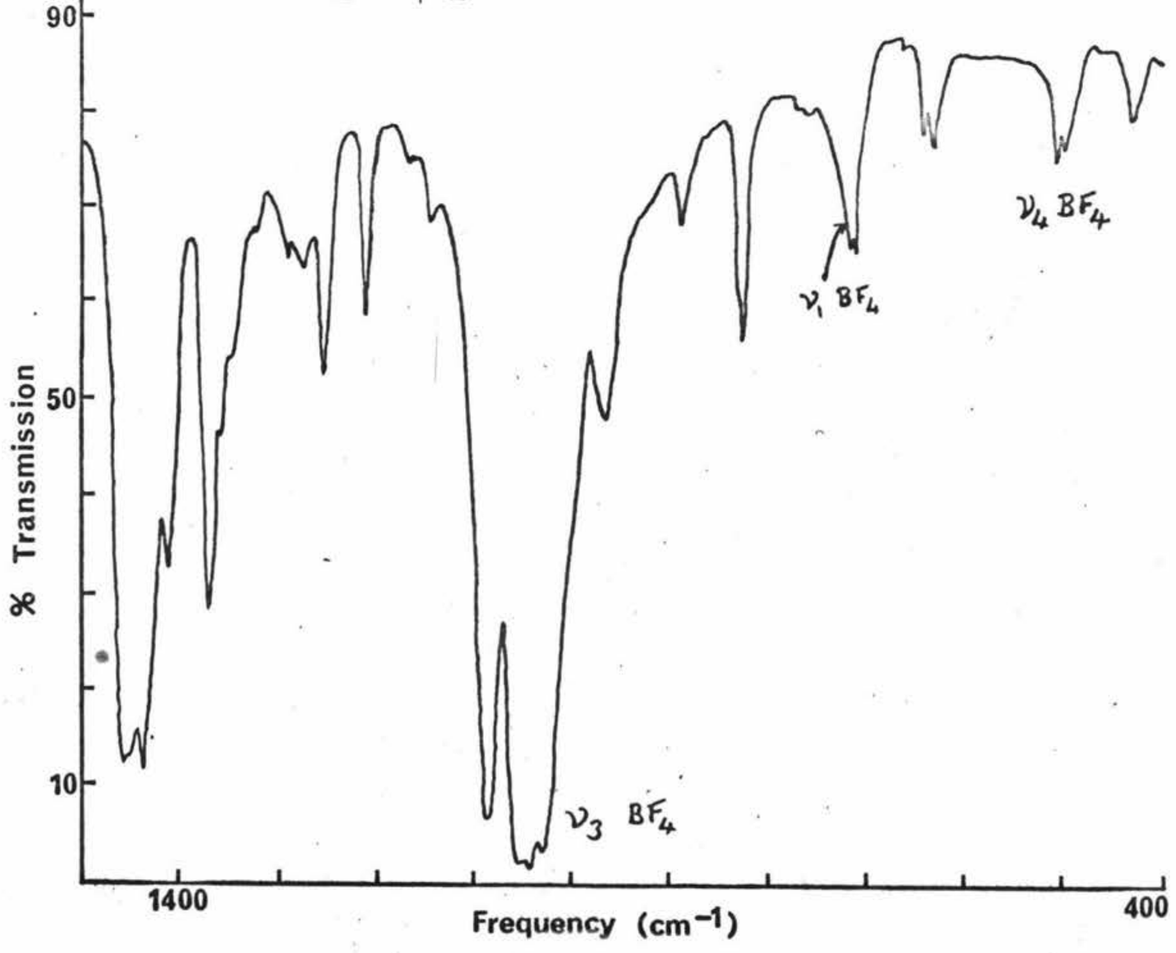
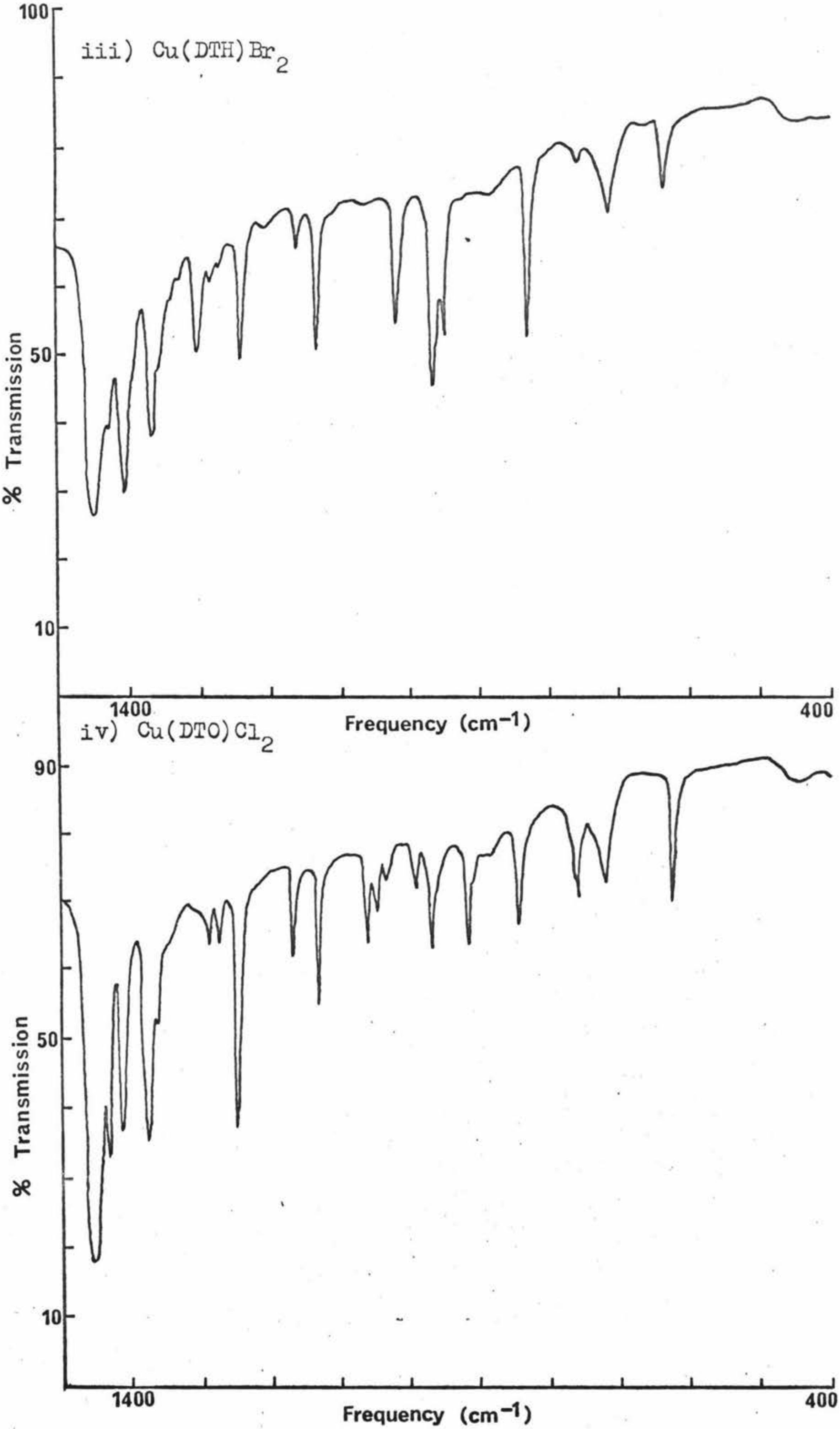


Figure 2.2b Infra-red Spectra Continued



an extra weak band at 768cm^{-1} in Cu(dien)$(BF_4)_2 \cdot H_2O$ which they assigned to the ν_1 mode of BF_4. They also found a broadening and splitting of the ν_3 mode at 1000cm^{-1}. It may be noted that previously infra-red inactive bands sometimes become infra-red active on coordination. They, therefore, attributed the extra band and splitting to be due to the semicoordination of BF_4. Procter et al[30] proposed that coordination lowers the symmetry of the free ion and hence the degeneracies of some modes are removed and the bands are split. This they found with $Cu(en)_2(BF_4)_2$, which has weakly coordinated BF_4 groups with Cu-F distances of 2.56Å. The infra-red spectral data is therefore, consistent with structure. This same pattern occurred in the infra-red spectrum of $Cu(DTO)_2(BF_4)_2$ which had broad peaks at 1055cm^{-1} and 1020cm^{-1}, a band at 522cm^{-1}, and a medium band at 763cm^{-1}. This pattern indicates that the complexes $Cu(DTO)_2(BF_4)_2$ and $Cu(DTH)_2(BF_4)_2$ may be isostructural.

The x-ray powder photographs show similar patterns of 2θ and d for $Cu(DTO)Cl_2$ and $Cu(DTO)Br_2$ indicating that these two compounds have very similar structures in the solid state. $Cu(DTH)Cl_2$ and $Cu(DTH)Br_2$ have similar patterns of 2θ and d indicating that they, may be isostructural. See table 2.3c for values of 2θ, d and relative intensities.

The far infra-red absorptions are recorded in Table 2.2a. From the spectrum of $Cu(DTH)_2(BF_4)_2$ it would appear that the ν(Cu-S) stretching frequencies may be in the range 253cm^{-1} to 296cm^{-1}. Some of the bands below approximately 277cm^{-1} in the complexes may be C-S-C deformations e.g. the

Table 2.3c

$Cu(DTO)Cl_2$				$Cu(DTO)Br_2$			
	2θ	d	Relative Intensity		2θ	d	Relative Intensity
1.	11.59	8.86	vs	1.	11.62	8.83	vs
2.	13.72	7.49	m-s	2.	12.65	7.52	vs
3.	14.07	7.30	vs	3.	15.00	6.85	vs
4.	15.14	6.79	vs	4.	18.15	5.67	m
5.	15.50	6.63	m-s	5.	20.19	5.10	m
6.	17.08	6.02	w	6.	20.53	5.02	w
7.	20.14	5.12	s	7.	22.40	4.61	w
8.	20.82	4.95	m	8.	25.50	4.05	w
9.	22.61	4.56	w	9.	26.46	3.91	vs
10.	23.04	4.48	m	10.	27.23	3.80	vs
11.	23.39	4.41	w	11.	29.08	3.56	w
12.	23.70	4.36	vw	12.	30.15	3.44	s
13.	24.21	4.26	vw	13.	30.50	3.40	m
14.	25.78	4.01	m	14.	31.37	3.31	w
15.	27.03	3.83	m-s	15.	32.00	3.245	vs
16.	27.28	3.79	vw	16.	32.62	3.185	m
17.	27.59	3.75	m-s	17.	33.09	3.14	m-s
18.	29.63	3.50	vw	18.	33.57	3.10	w
19.	30.00	3.46	m	19.	33.98	3.06	w
20.	30.44	3.41	w	20.	35.15	2.96	vs
21.	30.57	3.39	vw	21.	35.44	2.94	m-s
22.	30.87	3.36	vw	22.	35.88	2.90	s
23.	31.25	3.32	vw	23.	37.75	2.76	m
24.	32.00	3.245	vw	24.	38.14	2.74	w
25.	32.60	3.19	w	25.	39.11	2.67	m
26.	33.10	3.14	vw	26.	39.61	2.64	w
27.	33.37	3.12	w	27.	41.33	2.53	m
28.	33.69	3.09	vw	28.	42.12	2.49	vw
29.	33.97	3.06	vw	29.	42.70	2.46	w
30.	35.05	2.97	w-m	30.	43.30	2.42	w-m
31.	35.48	2.94	m	31.	43.76	2.40	vw
32.	35.97	2.90	vw	32.	44.07	2.38	w
33.	36.61	2.85	m-s	33.	44.53	2.36	vw
34.	37.62	2.77	w	34.	44.97	2.34	w-m
35.	38.55	2.71	w-m	35.	45.50	2.31	w
36.	38.67	2.70	w-m	36.	48.48	2.18	m
37.	42.43	2.47	w-m	37.	49.43	2.14	vw
38.	43.77	2.40	vw	38.	49.99	2.12	m
39.	44.18	2.38	m-s	39.	51.07	2.075	vw
40.	45.62	2.31	m	40.	52.28	2.030	m

d measured in A , 20 measured in
vs=very strong s=strong
m-s=medium to strong m=medium
w-m=weak to medium w=weak
vw=very weak
X-ray generator Philips PW 1011 using Philips Pw 1352 recording unit.

Table 2.3c continued.

$Cu(DTH)Cl_2$

	2θ	d	Relative Intensity
1.	14.30	7.18	s
2.	16.65	6.18	vs
3.	17.35	5.93	w–m
4.	19.27	5.34	w
5.	22.02	4.68	w
6.	22.60	4.56	w
7.	25.40	4.07	m
8.	26.20	3.95	vw
9.	26.64	3.88	vw
10.	27.57	3.75	w–m
11.	29.15	3.55	s
12.	30.21	3.43	vw
13.	31.31	3.31	w
14.	32.10	3.23	s
15.	32.35	3.21	vs
16.	32.66	3.18	s
17.	34.25	3.04	m
18.	36.72	2.84	vw
19.	38.40	2.72	m–s
20.	40.80	2.57	s
21.	41.31	2.54	w–m
22.	43.00	2.44	vw
23.	45.10	2.33	w
24.	45.37	2.32	w–m
25.	47.20	2.23	w
26.	47.65	2.21	w
27.	49.95	2.12	vs
28.	51.42	2.06	w
29.	53.25	1.99	w–m
30.	54.55	1.95	vw
31.	55.47	1.92	w
32.	57.90	1.85	vw
33.	58.18	1.84	w
34.	60.30	1.78	w
35.	61.60	1.75	w
36.	63.70	1.70	m

$Cu(DTH)Br_2$

	2θ	d	Relative Intensity
1.	13.29	7.73	w
2.	13.81	7.44	vs
3.	16.29	6.31	vs
4.	18.62	5.53	w–m
5.	19.89	5.18	w–m
6.	22.80	4.52	m–s
7.	23.15	4.46	vs
8.	23.77	4.34	vw
9.	25.55	4.05	vw
10.	26.73	3.87	w–m
11.	27.23	3.80	m–s
12.	27.75	3.73	m
13.	28.09	3.69	m
14.	29.60	3.50	w
15.	30.06	3.45	m
16.	30.67	3.38	m
17.	32.80	3.17	vs
18.	33.64	3.09	w–m
19.	34.45	3.02	m–s
20.	36.10	2.89	vw
21.	36.72	2.84	vw
22.	37.25	2.80	vw
23.	38.12	2.74	m–s
24.	39.15	2.67	w
25.	39.85	2.62	vw
26.	40.20	2.60	vw
27.	40.86	2.56	vs
28.	42.00	2.50	w
29.	42.58	2.46	vw
30.	43.23	2.43	w
31.	44.72	2.35	w–m
32.	46.48	2.27	vw
33.	46.60	2.26	vw
34.	47.24	2.23	w
35.	49.93	2.12	m–s
36.	52.03	2.04	w
37.	53.15	2.00	w
38.	53.72	1.98	w
39.	57.50	1.86	w
40.	57.91	1.85	w
41.	68.26	1.59	w

d measured in A
vs=very strong
m–s=medium to strong
w–m=weak to medium
vw=very weak

2θ measured in
s=strong
m=medium
w=weak

Table 2.2a Far Infra-red Absorptions

Compound	Instrument	Absorption Maxima (cm^{-1})		
$Cu(DTO)Cl_2$	IR20	312s^{a};302s^{a};	291s^{b};281s^{b};	(272m;269m)
	Int.		* 291s^{b};283m,sh^{b};	(275m;265w;243w;195w-m;182w-m;155m;102s;85s)
$Cu(DTO)Br_2$	IR20		291s^{b};278s^{b};	(275m;273m;270m;264m)
	Int.	+256s^{c};243vs^{c};		(279w,sh;272m,sh;173m;165m;132w-m;115w-m;107w; 75vs;62m)
$Cu(DTH)Cl_2$	IR20	308s^{a};	295s^{b};282s^{b};	(276m;263m)
	Int		* 291s^{b};284s^{b};	(276m-s;265m;257w;153m;83s,br;73m;63m;)
$Cu(DTH)Br_2$	IR20	256s^{c};	292s^{b};288s^{b};	(277m;263m)
	Int	257s,sh^{c};253s^{c};	‡	(265m,sh;241w-m;233m;163w;145m;85vs,br)
$Cu(DTH)_2(BF_4)_2$	IR20		296s^{b};288s^{b};	(281s;277s;269s,sh;265m)
	Int.			(275s;259m-s;253s,sh;79s,br)

s = strong m = medium w = weak vs = very strong w-m = weak to medium m-s = medium to strong
sh = shoulder br = broad

‡ instrument limitations as maximum frequency was 275 cm^{-1} ;
* instrument limitations as maximum frequency was 291 cm^{-1};
\+ a shoulder at 251 may be due to splitting of the 256 cm^{-1} band;
a refers to bands assigned as (Cu-Cl) stretching frequencies;
b refers to bands assigned as (Cu-S) stretching frequencies;
c refers to bands assigned as (Cu-Br) stretching frequencies.

bands at ≃259cm^{-1} which occurs as a medium Raman band at 257cm^{-1} in the free ligand (DTH)[31] may become infra-red active on chelation of the ligand. In the complex Cu(DTH)Cl_2 Flint and Goodgame [8] assigned a strong band at 308cm^{-1} as ν(Cu-Cl) stretch. They also recorded strong bands at 288cm^{-1} and 272cm^{-1} for the same complex. They also reported strong bands at 290cm^{-1}, 272cm^{-1} and 259cm^{-1} for $Cu(DTH)_2(ClO_4)_2$; and strong bands at 291cm^{-1}, 274cm^{-1} and 255cm^{-1} for $Cu(DTH)_2(BF_4)_2$ but did not assign these. Petillon et al [32] assigned bands in the region 272cm^{-1} to 310cm^{-1} as ν(Cu-S) stretch for the complexes CuL_2X where $L=C_3H_2S_3$ and X=Cl or Br. As a result of these considerations the ν(Cu-S) stretching frequencies appear to be in the range 296cm^{-1} to 280cm^{-1}. Lever and Ramaswamy [33] assigned bands in the range 294cm^{-1} - to 305cm^{-1} to ν(Cu-Cl) stretch for pyridine and substituted pyridine complexes, whose structures ranged from polymeric distorted octahedra with chlorine bridges to five coordinate structures containing both "long" and "short" Cu-X bonds for Cu(2-methylpyridine)$_2X_2$ (where X=Cl or Br) and the sixth coordination site being blocked by the 2-methyl group. Lever and Mantovani [34] assigned strong bands above 300cm^{-1} for copper(II) chloride complexes of N,N'-dialkylethylenediamines, Cu(sym-R_2-en)Cl_2 where R=methyl or ethyl groups, to be those of ν(Cu-Cl) stretching frequencies. Considering Cu(DTO)Cl_2 and Cu(DTH)Cl_2 it would appear that the ν(Cu-Cl) stretching frequencies may be tentatively assigned to 312cm^{-1} and 302cm^{-1} for Cu(DTO)Cl_2 and 308cm^{-1} for Cu(DTH)Cl_2. These assignments are also based on the fact that these are not observed in the analogous bromide complexes or the $Cu(L)_2(BF_4)_2$ complexes, where L=DTO or DTH. Lever and Ramaswamy [33] assigned bands in the region 218cm^{-1} to 255cm^{-1} as ν(Cu–Br) stretching frequencies for the bromo analogs of the above substituted pyridine complexes. Lever and Mantovani [34] assigned medium bands at 227cm^{-1} to 229cm^{-1} for the bromo analogs of their substituted ethylenediamine complexes as ν(Cu–Br) stretching frequencies. The strong bands at 256cm^{-1} (251cm^{-1}sh) and 243cm^{-1}in $Cu(DTO)Br_2$ and the strong bands at 257cm^{-1} and 253cm^{-1} in $Cu(DTH)Br_2$ may be assigned to ν(Cu–Br) stretching frequencies. These are assigned because of their intensity, their position in relation to those assigned by Lever and Mantovani,[34] and Lever and Ramaswamy [33] and their position in relation to the copper–chlorine stretches where the ratio $\nu(Cu–Br)/\nu(Cu–Cl) \simeq 0.8$

2.3 Conductivities and Molecular Weights

All the complexes were of low solubility, especially the bromides, and so only a limited amount of data was obtained. The conductivities were measured in nitromethane. The complexes $Cu(DTO)Br_2$ and $Cu(DTH)Br_2$ were not sufficiently soluble in nitromethane for molecular weight measurements, but were measured in methanol. The complexes $Cu(DTO)Cl_2$ and $Cu(DTH)Cl_2$ were sufficiently soluble in both nitromethane and methanol for molecular weight determinations. See Table 2.3a for results.

Table 2.3a Molecular Weights and Molar Conductivities.

Compound	Solvent	M.W.Obs.	M.W.Calc.	Λ^{x}
$Cu(DTO)Cl_2$	CH_3OH	286	284.75	61.50
	CH_3NO_2	266	284.75	10.92
$Cu(DTH)Cl_2$	CH_3OH	171	256.70	-
	CH_3NO_2	279	256.70	4.56
$Cu(DTO)Br_2$	CH_3OH	368	373.66	-
	CH_3NO_2	-	373.66	18.93
$Cu(DTH)Br_2$	CH_3OH	272	345.61	-
	CH_3NO_2	-	345.61	20.42
$Cu(DTH)_2(BF_4)_2$	CH_3NO_2	-	481.66	197.03

x = mhos cm^2

From the molecular weight data in Table 2.3a it appears that $Cu(DTO)Cl_2$ and $Cu(DTO)Br_2$ are monomeric in methanol, whilst the values for $Cu(DTH)Cl_2$ and $Cu(DTH)Br_2$ are unusually low. The low value for $Cu(DTH)Cl_2$ may be due to some dissociation of the chloro group and that of $Cu(DTH)Br_2$ may be due to its ease of reduction in solution (especially on heating). Both $Cu(DTO)Cl_2$ and $Cu(DTH)Cl_2$ appear to be monomeric in nitromethane solutions.

The molar conductivities of all the copper(II) complexes, except for the tetrafluoroborate, indicate that they are virtually non-electrolytes in nitromethane (the required value for a 1:1 electrolyte in nitromethane being in the range 70-90). The value for a 1:1 electrolyte in methanol is 100-130 indicating that $Cu(DTO)Cl_2$ is also a non-electrolyte in methanol. $Cu(DTH)_2(BF_4)_2$ is a 2:1 electrolyte in nitromethane indicating that the tetrafluoroborate groups are ionic in solution whereas the crystal structure shows that they are weakly coordinated in the solid state (see figure 2.2a).

Electronic Spectra

The electronic absorption maxima and some of the molar extinction coefficients are recorded in Table 2.3b. The solution spectra were recorded in acetonitrile and nitromethane. The solid electronic reflectance spectra was recorded on undiluted samples, except for $Cu(DTH)_2(BF_4)_2$ which was diluted with MgO.

In all complexes a ligand charge-transfer band was recorded in the range 42,700 cm^{-1} to 45,500 cm^{-1}. The free DTH ligand has a band at 43,100 cm^{-1} and DTO a band at 41,800 cm^{-1}, so a slight shift of these bands was observed on complexation.

In principle the maximum number of d-d transitions in the electronic spectrum of a copper(II) complex is four, however Hathaway [35] makes the comment that in practice very few complexes give any indication of more than two bands, and that most show only one broad band with occasionally a shoulder to the high or low energy side usually the lower. In Table 2.3b we see that all the complexes exhibit one band except for both the bromides which also contain a shoulder on the lower energy side of the main band. Lever and Mantovani [34] in their investigations of ethylenediamine complexes assign a shoulder at ≃14,000 cm^{-1} to the $z^2 \longrightarrow x^2-y^2$ transition. This is in agreement with theory for a slightly tetragonally distorted octahedral symmetry where this transition requires less energy than that of the other three possible transitions ($xy \longrightarrow x^2-y^2$, $xz \longrightarrow x^2-y^2$, $yz \longrightarrow x^2-y^2$). Lever and Mantovani [36] stated the most strongly coordinating axial ligand (such as halogens or pseudohalogens) will tend to coordinate to the copper atom

Table 2.3b Ultra-violet and Visible Absorption Bands with Extinction Coefficients[a]

Compound	Other Bands (cm^{-1})			d-d Transitions (cm^{-1})	State of Compound
Cu(DTO)Cl_2	26,800vi^e	22,750(1900)		13,800(285)	b
	45,000;38,700;29,000(2844)	22,700(1118)		14,000^f	c
	27,800	23,400		12,750	d
Cu(DTH)Cl_2	26,800vi^e	23,000(2100)		13,650(301)	b
	45,500;38,900;28,900(4430)	23,100(1420)		14,000^f	c
	27,400	23,000		12,350	d
Cu(DTO)Br_2	26,800vi^e		18,600(972)	15,600(796);13,800sh(500)	b
	44,500;37,400;28,200(2050)	24,400sh(1000)		16,000(800);14,000sh^f	c
		22,700	18,800	12,800	d
Cu(DTH)Br_2	26,800vi^e		18,800(860)	15,650(643);14,300sh(565)	b
	43,650;38,000;28,200(2100)	24,700(1175)		15,900(400);14,000sh^f	c
Cu$(DTH)_2(BF_4)_2$		23,100(4840)		18,800(920)	b
	42,700;35,700vw,sh	25,100(1090)		16,100(175)	c
		22,800		18,700	d

a values in parenthesis b = nitromethane solution c = acetonitrile solution d = solid vi = very intense
e these bands were asymmetric indicating that the solvent had started to absorb in this region and, therefore, the bands are incomplete
f because of instrument limitations these bands were not observed in their entirety
vw = very weak sh = shoulder

and form tetragonally distorted octahedra. When the axial ligand is perchlorate, nitrate, or tetrafluoroborate, (ions which are generally regarded as being only weakly coördinating) coordination may occur to yield strongly tetragonally distorted octahedra. As the axial ligand strength weakens, be it for steric or electronic reasons, the in-plane strength increases due to increased involvement of the copper atom's orbitals with the in-plane ligands. As a result the crystal field splitting energies increase and hence the d-d transitions have greater energies. Therefore, the highest energies of d-d bands are observed with the weakly coordinating axial ligands and the position of this band is a useful indication of the degree of tetragonal distortion.

$Cu(DTH)_2(BF_4)_2$ has a d-d band at 18,700cm^{-1} in the solid state. This is comparable to 19,510cm^{-1} for $Cu(en)_2(BF_4)_2$, 18,790cm^{-1} for $Cu(sym\text{-}Me_2\text{-}en)_2(BF_4)_2$, and 18,650cm^{-1} for $Cu(sym\text{-}Et_2\text{-}en)_2(BF_4)_2$ in the solid state reported by Lever and Mantovani [36]. The crystal structures of both $Cu(DTH)_2(BF_4)_2$ and $Cu(en)_2(BF_4)_2$ [36] are similar in that both are tetragonally distorted. The d-d band decreases slightly in energy in nitromethane, but substantially in acetonitrile. This indicates that solvent molecules are replacing the tetrafluoroborate ions and coordinating more strongly and thus decreasing the in-plane interactions as stable acetonitrile complexes with copper(II) salts have been prepared e.g. $CuX_2(CH_3CN)_n$ where n=⅔, 1, or 2. [37]

The solid reflectance spectra of $Cu(DTO)Cl_2$, $Cu(DTH)Cl_2$, and $Cu(DTO)Br_2$ show d-d bands in the region 12,350cm^{-1} to 12,800cm^{-1} indicating that there is much less tetragonal distortion in these complexes than in $Cu(DTH)_2(BF_4)_2$ and, therfore, that these compounds may be polymeric in the solid state. As these compounds seem to be monomeric in solution, it appears as though the solvent molecules are coordinated in solutions of the above complexes.

Copper sulphur charge transfer bands have been assigned in the range 23,400 cm^{-1} to 25,000 cm^{-1} for substituted thiourea complexes of copper(II) perchlorates [38], 22,900 cm^{-1} to 23,800 cm^{-1} for copper(II)-bis(diethyldithiocarbamate) [39,40] and 23,000 cm^{-1} for copper(II)-bis(di-isopropyldithiocarbamate) [39]. On this basis the bands in the region 22,700 cm^{-1} to 25,100 cm^{-1} may be assigned to copper sulphur charge transfer bands for the copper(II) complexes of DTO and DTH. Halogen to copper charge transfer bands have not been reported for complexes containing sulphur ligands. However, chlorine to copper charge transfer bands have been reported for the complexes $Cu(N\frown N)_2Cl_2$ [41] (where N⌒N is ethylenediamine, sym-dimethylethylenediamine, or sym-diethylethylenediamine) in the range 36,800 cm^{-1} to 33,500 cm^{-1}. The following chlorine to copper charge transfer bands have also been reported [41] 18,000 cm^{-1} for $CuCl_2$, 22,000 cm^{-1} to 25,000 cm^{-1} for $CuCl_4^{2-}$, and 24,200 cm^{-1} for $CuCl_5^{3-}$. On this basis the solid reflectance bands at 27,800 cm^{-1} for $Cu(DTO)Cl_2$ and 27,400 cm^{-1} for $Cu(DTH)Cl_2$ may be assigned to chlorine to copper charge transfer bands. The bands at 35,700 cm^{-1} to 38,900 cm^{-1} do not appear to be halide to copper charge transfer bands as a band at 35,700 cm^{-1} is present in $Cu(DTH)_2(BF_4)_2$. For the compounds CuL_2X_2 (where L=substituted pyridine and X=Br)

Tong and Brewer [42] have assigned bromine to copper charge transfer bands at 27,700cm^{-1} to 27,900cm^{-1}.In Table 2.3b bromine to copper charge transfer bands for the complexes Cu(DTO)Br_2 and Cu(DTH)Br_2 can not be assigned with confidence, however, in acetonitrile solutions bands at 28,200cm^{-} are tentative assignments.

Studies of the copper(II) complexes both in the solid state and in solution show that the compounds may have polymeric octahedral structures.

2.4 Experimental

3,6-dithiaoctane (DTO) was supplied by K and K Laboratories and Wateree Chemical Company. 2,5-dithiahexane was supplied by K and K Laboratories and Chemical Procurements Ltd. Both ligands were found to be pure, using proton nuclear magnetic resonance spectroscopy at high power and high resolution, and used without any further purification.

Solvents:

acetone was dry Analar grade of >99% purity;
ethanol was absolute after redistillation;
methanol was absolute after redistillation;
diethyl ether was redistilled and dried over sodium wire;
nitromethane was redistilled over phosphorous pentoxide;
2,2-dimethoxypropane (DMP) was kept over a molecular seive;
triethylorthoformate (TEOF) was supplied by Hopkin and Williams and used without further purification.

For the reactions all solvent volumes were kept to a minimum.

$CuCl_2.2H_2O$, CuO, $Cu(NO_3)_2.3H_2O$, and HBF_4 were laboratory reagent grade supplied by B.D.H. Ltd and used without further purification.

$CuBr_2$ was recrystallised from absolute ethanol.

Syntheses

$Cu(BF_4)_2.6H_2O$ was prepared by reacting HBF_4 with CuO until no further reaction occurred on addition of CuO to HBF_4. The resulting blue solution was filtered, and concentrated to low volume on a steam bath, and then allowed to cool. The resulting blue crystals were filtered off on a vacuum pump and dried under vacuum.

Dibromo(3,6-dithiaoctane)copper(II) $Cu(DTO)Br_2$

This compound could not be isolated from solution and was therefore, prepared by a method used by Carlin and Weissburger [7] in their syntheses of cobalt(II) complexes of DTO. 223mg (1.0mmoles) of finely ground $CuBr_2$ was placed in a 5ml beaker and excess DTO (5.0mmoles=0.5mls) added to cover the $CuBr_2$. This mixture was left to react for 15 minutes. The dark brown product was filtered to remove the excess DTO, washed with dry diethyl ether and dried under vacuum. The yield was 95% and the m.p. = 129-131° C. Analytical results for $CuBr_2C_6H_{14}S_2$: calculated %C=19.29, %H=3.78, %Br=24.90; observed %C=19.43, %H=3.58, %Br=26.48.

Dichloro(3,6-dithiaoctane)copper(II) Cu(DTO)Cl_2

852mg (5.0mmoles) $CuCl_2.2H_2O$ were dissolved in acetone and 752mg (5.0mmoles) DTO were added to form a dark green precipitate, which was filtered off, washed with dry diethyl ether, and dried under vacuum. The yield was 90% and the m.p. 124-126° C (c.f. literature value of 126° C obtained by Tschugaeff). Analytical results for $C_6H_{14}S_2CuCl_2$: calculated %C=25.31, %H=4.96, %Cl=24.90; observed %C =25.44, %H=5.05, %Cl=26.48. Tschugaeff and Subbotin first prepared this compound.[17]

Dinitrato(3,6-dithiaoctane)copper(II) monohydrate

Cu(DTO)$(NO_3)_2.H_2O$

242mg (1.0mmoles) $Cu(NO_3)_2.3H_2O$ were dissolved in DMP and 150mg (1.0mmoles) DTO were added dropwise to give a dark green precipitate. This was filtered off, washed with dry diethyl ether, and dried under vacuum. An oil resulted when the compound was prepared in either acetone or ethanol. The yield was 56% and the m.p. was not obtained. Analytical results for $CuN_2O_7C_6H_{16}S_2$: calculated %C=20.25, %H=4.53, %N=7.87; observed %C=20.04, %H=4.62, %N=6.92. The nitrogen figure was obtained after the compound had started to change colour to a lighter green. The compound appears to be very hygroscopic.

Bis(3,6-dithiaoctane)copper(II)tetrafluoroborate

$Cu(DTO)_2(BF_4)_2$

173mg (0.5mmoles) $Cu(BF_4)_2.6H_2O$ were dissolved in TEOF and refluxed until the solution changed from blue to green in colour. The solution was then allowed to cool. 150mg (1.0 mmoles) DTO was added slowly and a brown precipitate formed. The precipitate was filtered off, washed with dry diethyl ether, and dried under vacuum. The yield was 60% and the m.p. was not obtained. Analytical results for $CuB_2F_8C_{12}H_{28}S_4$: calculated %C=26.80, %H=5.25; observed %C=26.88, %H=5.27. This compound is not stable and had completely decomposed in three weeks.

Dichloro(2,5-dithiahexane)copper(II) $Cu(DTH)Cl_2$

This compound was prepared by Bergen's method giving a 95% yield, and m.p.=125°C c.f. 130-130.5°C by Morgan and Ledbury. Morgan and Ledbury [6] used a water-alcohol medium and HCl to prevent reduction to Cu(DTH)Cl. $Cu(DTH)Cl_2$ when dissolved in water loses all colour immediately suggesting reduction to the Cu(I) compound. However, when acetone is used as a solvent no reduction occurs and the yield is four times that of Morgan and Ledbury. These researchers also claim that the solid compound shows sign of reduction but no sign of reduction was seen after 12 months of storage. Flint and Goodgame [8] did not report their preparation of this compound.

Dibromo(2,5-dithiahexane)copper(II) $Cu(DTH)Br_2$

335mg (1.5mmoles) $CuBr_2$ were dissolved in ethanol and 183mg (1.5mmoles) DTH added to form a dark brown precipitate. The precipitate was filtered off, washed with dry diethyl ether, and dried under vacuum. The yield was 72% and the m.p. 130–131° C. Analytical results for $CuBr_2C_4H_{10}S_2$: calculated %C=13.90, %H=2.92, %Br=46.24; observed %C=13.98, %H=3.02, %Br=47.34.

2.5 Complexes of 3,6-dithiaoctane-3,6-dioxide (DTO-O_2)

On standing, the complex Cu(DTO)$(NO_3)_2.H_2O$ changed colour from dark green to light green while it absorbed water, yet it remained in a solid state. An infra-red spectrum of the light green compound contained the bands due to Cu(DTO)$(NO_3)_2.H_2O$, but with much stronger and broader water bands, and two extra bands in the region 1200 cm^{-1} to 1300 cm^{-1}. These bands were thought to be ν(S=O) stretching frequencies. It was, therefore, decided to prepare some complexes with 3,6-dithiaoctane-3,6-dioxide and compare their spectra with those of the above compound.

The complexes prepared were; Cu(DTO-O_2)Cl_2, Cu(DTO-O_2)$(NO_3)_2$, Cu(DTO-O_2)$_2$$(BF_4)_2$ and Cu(DTO-O_2)$_2$$(PF_6)_2$. These syntheses were very difficult being sensitive to solvent, extremely sensitive to the presence of water, having low yields, and the ligand was prone to precipitating out at high concentrations. However, Cu(DTO-O_2)Cl_2, Cu(DTO-O_2)$(NO_3)_2$ and Cu(DTO-O_2)$_2$$(PF_6)_2$ gave good analyses, whilst that of Cu(DTO-O_2)$_2$$(BF_4)_2$ showed the presence of some free ligand. This was found to be correct upon examination of the sample under a microscope. For experimental and analytical details see the section on syntheses.

The disulphoxide (DTO-O_2) was prepared by oxidising DTO using hydrogen peroxide and glacial acetic acid (see section on syntheses for details) to get a racemic mixture of isomers which were not separated. According to Bell and Bennett [42] two isomers of 2,5-dithiahexane-2,5-dioxide (DTH-O_2) can be prepared and separated by fractional crystallisation. These isomers have melting points 30° C apart. As the melting point for DTO_O_2 was over the range 117° C to 133° C it is reasonable to conclude that the compound separated was a racemic mixture of the isomers of DTO_O_2.

The infra-red spectra showed a shift of the strong broad ν(S=O) stretching frequencies at 1019 cm^{-1} and 1047 cm^{-1} in the free ligand to between 900 cm^{-1} and 950 cm^{-1} in the prepared complexes. Wayland et al [43] in their studies of platinum and palladium complexes of various sulphoxides, including $DTHO_2$, showed that this shift to lower frequencies corresponded to bonding through the oxygen atom whilst shifts to a higher frequency between 1100 cm^{-1} and 1150 cm^{-1} corresponded to bonding through the sulphur atom. This is conclusive evidence that DTO_O_2 is bonded through the oxygen atom for the above complexes. No further physical measurements were made on these complexes.

When the infra-red spectrum of the original light green $Cu(DTO)(NO_3)_2.H_2O$ compound was compared with those of the above prepared complexes no conclusions could be made about the two extra bands in the 1200 cm^{-1} to 1250 cm^{-1} region for the light green $Cu(DTO)(NO_3)_2.H_2O$ compound.

Syntheses

For a description of the solvents used see Chapter 2.4 Glacial acetic acid, 30% hydrogen peroxide, and NH_4PF_6 were all supplied by B.D.H. Ltd and used without further purification.

3,6-dithiaoctane-3,6-dioxide DTO-O_2

11.4g (0.76moles) 3,6-dithiaoctane were added slowly to a stirred solution of 100ml glacial acetic acid (CH_3COOH) with 20g of 30% hydrogen peroxide (H_2O_2). The solution was then left to stand for 15 minutes to ensure a complete reaction, and then evaporated to dryness on a steam bath. The resulting crystalline product was recrystallised from ethanol. The yield was 52% and the m.p. was 117-133°C.

Dinitrato(3,6-dithiaoctane-3,6-dioxide)copper(II)

Cu(DTO-O_2)$(NO_3)_2$

241mg (1.0mmoles) $Cu(NO_3)_2.3H_2O$ was dissolved in triethylorthoformate (TEOF). 182mg (1.0mmoles) DTO-O_2 was dissolved in acetone containing 2-3mls of ethanol and this solution added to the former and heated until a blue precipitate appeared. The precipitate was filtered off, washed with dry diethyl ether, and dried under vacuum. On cooling a second blue precipitate formed which was also filtered off, washed with dry diethyl ether, and dried under vacuum. The infrared spectra of these two compounds were identical, but the first precipitate was the purer product, and therefore used for analysis. The second contained some free ligand (observed under a microscope). The yield using the first precipitate was 23% and the m.p. was 184-185°C.
Analytical results for $C_6H_{14}S_2O_8N_2Cu$: calculated %C=19.44, %H=3.82, %N=7.58; observed %C=19.92, %H=3.98, %N=7.31.

Dichloro(3,6-dithiaoctane-3,6-dioxide)copper(II)

$Cu(DTO\text{-}O_2)Cl_2$

170mg (1.0mmoles) $CuCl_2.2H_2O$ were dissolved in ethanol and 5mls of 2,2-dimethoxypropane (DMP) added. 182mg (1.0mmoles) $DTO\text{-}O_2$ was added as an ethanol solution. The resulting solution was heated until a yellow colour appeared and an extra 15mls DMP added. Further heat was applied until a yellow-green precipitate appeared. The precipitate was filtered off, washed with DMP and dried under vacuum. The yield was 5% and the m.p. was 174-176°C. Analytical results for $C_6H_{14}S_2O_2Cl_2Cu$: calculated %C=22.75, %H=4.46, %Cl=22.39; observed %C=23.25, %H=4.62, %Cl=21.97.

Bis(3,6-dithiaoctane-3,6-dioxide)copper(II)hexafluorophosphate

$Cu(DTO\text{-}O_2)(PF_6)_2$

174mg (0.5mmoles) $Cu(BF_4)_2.6H_2O$ were dissolved in acetone and an equal amount of DMP added. A second solution containing 182mg (1.0mmoles) $DTO\text{-}O_2$ dissolved in acetone with 2-3mls ethanol was added to the first solution. To the resulting solution was added 165mg (1.0mmoles) ammonium-hexafluorophosphate (NH_4PF_6) as an acetone solution. The solution was heated until a blue precipitate appeared, which was filtered off, washed with hot acetone, and dried under vacuum. The yield was 14% and the compound discoloured at 190-195°C. Analytical results for $C_6H_{14}S_2O_2P_2F_{12}Cu$: calculated %C=22.45, %H=4.40; observed %C=22.03, %H=4.09.

Bis(3,6-dithiaoctane-3,6-dioxide)copper(II)tetrafluoroborate

$Cu(DTO\text{-}O_2)_2(BF_4)_2$

348mg (1.0mmoles) $Cu(BF_4)_2.6H_2O$ were dissolved in DMP and heated until the solution changed colour from blue to green. To this solution was added 364mg (2.0mmoles) $DTO\text{-}O_2$ in acetone containing 2-3mls of ethanol. The resulting solution was heated until a blue precipitate appeared. The solution was allowed to cool, before the blue precipitate was filtered off, washed with DMP, and dried under vacuum. The yield was 11% but contained some free $DTO\text{-}O_2$. The m.p. was not determined because of the presence of ligand. Analytical results for $C_6H_{14}S_2O_2B_2F_8Cu$: calculated %C: 23.95, %H=4.69; observed %C=24.32, %H=5.74.

CHAPTER 3

COPPER(I) COMPLEXES OF 2,5-DITHIAHEXANE AND 3,6-DITHIAOCTANE

Many complexes between copper(I) halides and neutral ligands, of general formula $(CuX)_nL_m$ are known. Often as in the case of the series $(CuX)_n(DPM)_m$ [45] (DPM=bis (diphenylphosphino) methane) they exist in different stoichiometric ratios, for the same X and L species, and show rather intriguing structures. Camus et al on the basis of known structures and their own results suggested a simple scheme for the rationalisation of the $(CuX)_nL_m$ structures known to them. They also commented that the behaviour of sulphur containing ligands could not be rationalised in the same way, because sulphur is able to coordinate one or more copper atoms in the same complex giving compounds of identical stoichiometry but with different structures.[46]

3.11 Syntheses and Characterisation

In my investigations I prepared the following copper(I) complexes; Cu(DTH)X where X=Cl, Br, or I; Cu(DTO)X where X=I, or SCN; $Cu(DTO)_2BF_4$; $(CuX)_2DTO$ where X=Cl or Br.

For the complexes Cu(DTH)X where X=Cl or Br, $(CuX)_2DTO$ where X=Cl or Br, and $Cu(DTO)_2BF_4$ the appropriate copper(II) complex was prepared in solution and then reduced to the copper(I) complex using hypophosphorous acid. It was found that using this method of reduction produced pure compounds. $Cu(DTO)_2BF_4$ was soluble in the solvent used and therefore, diethyl ether was added to promote precipitation. The yield was very low but the crystals obtained were used for a single crystal x-ray analysis.[27] The preparations of Cu(DTH)Cl and $(CuCl)_2$DTO were repeated with increased solvent volumes to induce slower precipitation and, therefore, better crystals for an x-ray structure analysis. This proved to be the case with Cu(DTH)Cl where the crystal structure will be determined in this laboratory. $(CuCl)_2$DTO did not form crystals suitable for a crystal structure but the compound was more crystalline. $(CuBr)_2$DTO was formed as plate-like crystals when a dilute solution of the copper(II) bromide complex was left to stand. CuLI, where L= DTH or DTO, was prepared in a pure form by reacting the copper(II) chloride complexes with lithium iodide. Cu(DTO)SCN was prepared via Cu(DTO)$(NO_3)_2$ which was reacted with potassium thiocyanate to give a dark red solution containing the copper(II) thiocyanate complex which could not be isolated in a pure form and a white precipitate of potassium nitrate. The red solution was reduced using hypophosphorous acid to give crystalline Cu(DTO)SCN but the crystals are not good enough for single crystal x-ray studies. For experimental details see section 3.2 of this chapter.

The analytical data was obtained from the microanalytical laboratory at Otago University with good results for the DTO complexes using normal techniques. The DTH complexes gave low carbon and hydrogen figures using the normal cycles but it was found that by cooling the sample prior to the commencement of the combustion cycle good results were obtained. This may account for the low figures obtained by Bratermann and Wilson[14] who suggested that Cu(DTH)Cl was unstable losing DTH in normal atmospheric conditions. We have found, however, that all the copper(I) complexes of DTH and DTO are stable in air at room temperature, For details of analyses see section 3.2 of this chapter.

The mass spectrum was attempted on Cu(DTH)Cl but only a strong ligand band was observed with the ligand being pulled off under high vacuum.

The molecular weights (by vapour pressure osmometry) and conductivities of these compounds were measured in acetonitrile (methyl cyanide). The molecular weights gave results indicating that both ligands were displaced by the acetonitrile. On this basis the conductivities were also taken to be meaningless for the above complexes. This was most unfortunate as these complexes were sufficiently soluble only in this solvent. As a result of the mass spectral data and the solution data it appears that the dithioether ligands are very weakly coordinated and the complexes are not stable.

X-ray powder photographs showed that the structures of $(CuCl)_2DTO$ and $(CuBr)_2DTO$ are quite different thus confirming the infra-red data. The diffraction pattern for Cu(DTO)I is also different to those of $(CuCl)_2DTO$ and $(CuBr)_2DTO$ as would be expected. The x-ray powder photographs for Cu(DTH)Cl and Cu(DTH)Br showed different patterns of 2θ and d indicatingthat the structure may not be the same. This is in agreement with the far infra-red data. The Cu(DTH)Br and Cu(DTH)I complexes however have very similar 20 and d values and this is indicative of similar structures. See Table 3.1f for values of 2θ, d and relative intensities.

Table 3.1f

$[(CuCl)_2DTO]_n$

	2θ	d	Relative Intensity
1.	10.95	9.37	w
2.	12.10	8.48	vs
3.	17.03	6.04	s
4.	17.97	5.73	vw
5.	21.91	4.71	w
6.	24.23	4.26	m-s
7.	27.11	3.82	s
8.	27.57	3.75	w
9.	36.68	2.84	s
10.	38.71	2.70	s
11.	40.68	2.57	vw
12.	41.02	2.55	vw
13.	44.27	2.37	vw
14.	46.82	2.25	w
15.	49.19	2.15	w
16.	49.60	2.13	s
17.	50.81	2.08	vw
18.	50.95	2.08	vw
19.	51.85	2.07	w
20.	52.60	2.02	w
21.	55.84	1.91	vw
22.	58.12	1.84	vw
23.	63.15	1.71	w

$[(CuBr)_2DTO]_n$

	2θ	d	Relative Intensity
1.	7.50	13.68	m
2.	11.80	8.70	m
3.	12.05	8.52	s
4.	12.44	8.26	vs
5.	14.98	6.86	m
6.	15.74	6.53	m
7.	21.53	4.79	vw
8.	22.62	4.56	w
9.	23.41	4.41	vw
10.	27.20	3.80	w
11.	27.90	3.71	vw
12.	28.25	3.66	vw
13.	29.48	3.51	vw
14.	30.15	3.44	vw
15.	30.37	3.41	vw
16.	33.53	3.10	w-m
17.	34.70	3.00	w
18.	35.20	2.96	w
19.	35.75	2.91	m
20.	36.65	2.84	w
21.	37.42	2.79	vw
22.	37.83	2.76	vw
23.	39.35	2.66	vw
24.	43.80	2.40	vw
25.	45.80	2.30	w
26.	46.30	2.27	vw
27.	47.42	2.22	vw
28.	47.90	2.20	vw
29.	48.75	2.17	vw
30.	49.41	2.14	vw
31.	50.89	2.08	vw
32.	52.12	2.04	w

d measured in A
vs=very strong
m-s=medium to strong
w-m=weak to medium
vw=very weak

20 measured in
s=strong
m=medium
w=weak
Instrument setting ;
$4/10^2/2/0$

Table 3.1f continued

Cu(DTO)I

	2θ	d	Relative Intensity
1.	12.02	8.54	m
2.	12.95	7.93	vw
3.	13.34	7.70	w
4.	14.33	7.17	vs
5.	17.73	5.80	w–m
6.	18.36	5.61	vw
7.	19.32	5.33	vw
8.	19.58	5.26	w–m
9.	23.65	4.36	w–m
10.	24.05	4.29	w–m
11.	24.87	4.15	m
12.	25.64	4.03	w
13.	26.72	3.87	w–m
14.	28.15	3.67	vw
15.	30.13	3.44	w
16.	32.40	3.20	vw
17.	36.40	2.86	vw
18.	37.09	2.81	vw
19.	37.44	2.79	m
20.	38.67	2.70	vw
21.	39.35	2.66	vw
22.	40.60	2.58	w
23.	41.86	2.50	vw
24.	43.77	2.40	vs
25.	44.30	2.37	w
26.	45.60	2.31	vw
27.	46.78	2.25	vw
28.	49.00	2.16	vw
29.	51.83	2.05	vw
30.	59.54	1.80	vs
31.	59.66	1.79	vs

[Cu(DTH)I]$_n$

	2θ	d	Relative Intensity
1.	12.77	8.04	vs
2.	13.00	7.90	s
3.	13.35	7.69	m–s
4.	16.80	6.12	s
5.	17.75	5.80	m
6.	18.20	5.65	m
7.	20.03	5.14	vw
8.	25.37	4.07	w
9.	25.59	4.04	m
10.	26.08	3.96	m–s
11.	26.80	3.63	s
12.	28.50	3.63	s
13.	29.05	3.57	w–m
14.	29.74	3.48	w
15.	30.58	3.39	vw
16.	31.60	3.28	s
17.	33.90	3.07	w–m
18.	34.00	3.06	w–m
19.	34.33	3.03	w
20.	36.30	2.87	vw
21.	38.75	2.70	w
22.	39.55	2.64	w
23.	39.67	2.63	w
24.	41.00	2.55	w
25.	41.70	2.51	vw
26.	42.80	2.45	vw
27.	44.80	2.35	vw
28.	47.70	2.21	m

d measured in A
vs=very strong
m–s=medium to strong
w–m=weak to medium
vw=very weak
Instrument Setting for DTO complex: 4/10^2/2/0

20 measured in
s=strong
m=medium
w=weak
Instrument setting DTH complex 2/10^2/2/0

Table 3.1f continued

Cu(DTH)Cl

	2θ	d	Relative Intensity
1.	13.66	7.52	vs
2.	14.00	7.34	s
3.	16.77	6.13	m–s
4.	20.70	4.98	w
5.	27.34	3.78	vw
6.	28.00	3.69	vs
7.	34.01	3.06	vs
8.	41.50	2.52	m
9.	44.55	2.36	w
10.	50.00	2.12	s
11.	50.90	2.08	s
12.	56.25	1.90	w–m
13.	56.37	1.89	w–m
14.	57.56	1.86	s
15.	57.65	1.85	s
16.	59.88	1.79	w
17.	78.20	1.42	m
18.	78.37	1.41	w

$[Cu(DTH)Br]_n$

	2θ	d	Relative Intensity
1.	13.05	7.87	vs
2.	13.20	7.78	vs
3.	13.70	7.50	m
4.	16.43	6.26	vw
5.	18.06	5.70	s
6.	18.70	5.50	vs
7.	20.50	5.03	w–m
8.	21.60	4.77	vw
9.	26.00	3.98	vw
10.	26.22	3.94	s
11.	26.51	3.90	vs
12.	27.50	3.76	m
13.	29.65	3.50	vw
14.	30.90	3.36	vw
15.	31.18	3.33	w
16.	31.45	3.30	vw
17.	32.00	3.24	w–m
18.	33.17	3.13	vw
19.	33.55	3.10	vw
20.	33.91	3.07	vw
21.	37.42	2.79	vw
22.	37.61	2.77	vw
23.	37.90	2.75	m–s
24.	39.77	2.63	s
25.	40.20	2.60	s
26.	40.82	2.56	vw
27.	41.35	2.53	vw
28.	41.88	2.50	vw
29.	42.27	2.48	vw
30.	43.52	2.41	vw
31.	46.59	2.26	vw
32.	48.89	2.16	vw

d measured in A
vs=very strong
m–s=medium to strong
w–m=weak to medium
vw=very weak

20 measured in
s=strong
m=medium
w=weak

3.12 Infra-red Spectra

The crystal structure of bis(3,6-dithiaoctane)copper(I)-tetrafluoroborate has been determined in this laboratory by Norris [27] . This structure shows that the DTO ligand is chelated (see figure 3.1a). The infra-red spectrum in the range 1600 cm^{-1} to 600 cm^{-1} for Cu(DTO)$_2$BF$_4$ shows four extra ligand bands at 1300m, 1286m, 916s, 840s when compared to that of the free ligand. All the other copper(I)dithiaoctane complexes, except for dichloro(3,6-dithiaoctane)dicopper, (CuCl)$_2$DTO, show a very similar pattern. (CuCl)$_2$DTO shows a much simpler spectrum, very similar to that of the free ligand. This indicates that the ligand may be bridging. See figure 3.1b.

When chelated it is impossible for a disubstituted ethane e.g. ethylenediamine , to have the trans conformation. Broderson [47] analysed the infra-red spectrum of solid Hg(en)Cl$_2$ and concluded from the simplicity of the spectrum that the ligand has the trans conformation. This implies that the complex has a bridging ethylenediamine. This was shown to be correct by x-ray analysis [47] . Powell and Sheppard [48] have studied the infra-red spectrum of a bridging ethylenediamine in the complex (C$_2$H$_4$)Cl$_2$PtenPtCl$_2$-(C$_2$H$_4$). After the ethylene modes were subtracted the spectrum was found to be much simpler than that of Pt(en)Cl$_2$, which contains chelated ethlenediamine with the gauche conformation. They concluded that the bridging ethylenediamine had the trans conformation.

Figure 3.1a Perspective View of Cu(DTO)$_2$BF$_4$ [27]
Where DTO=3,6-dithiaoctane

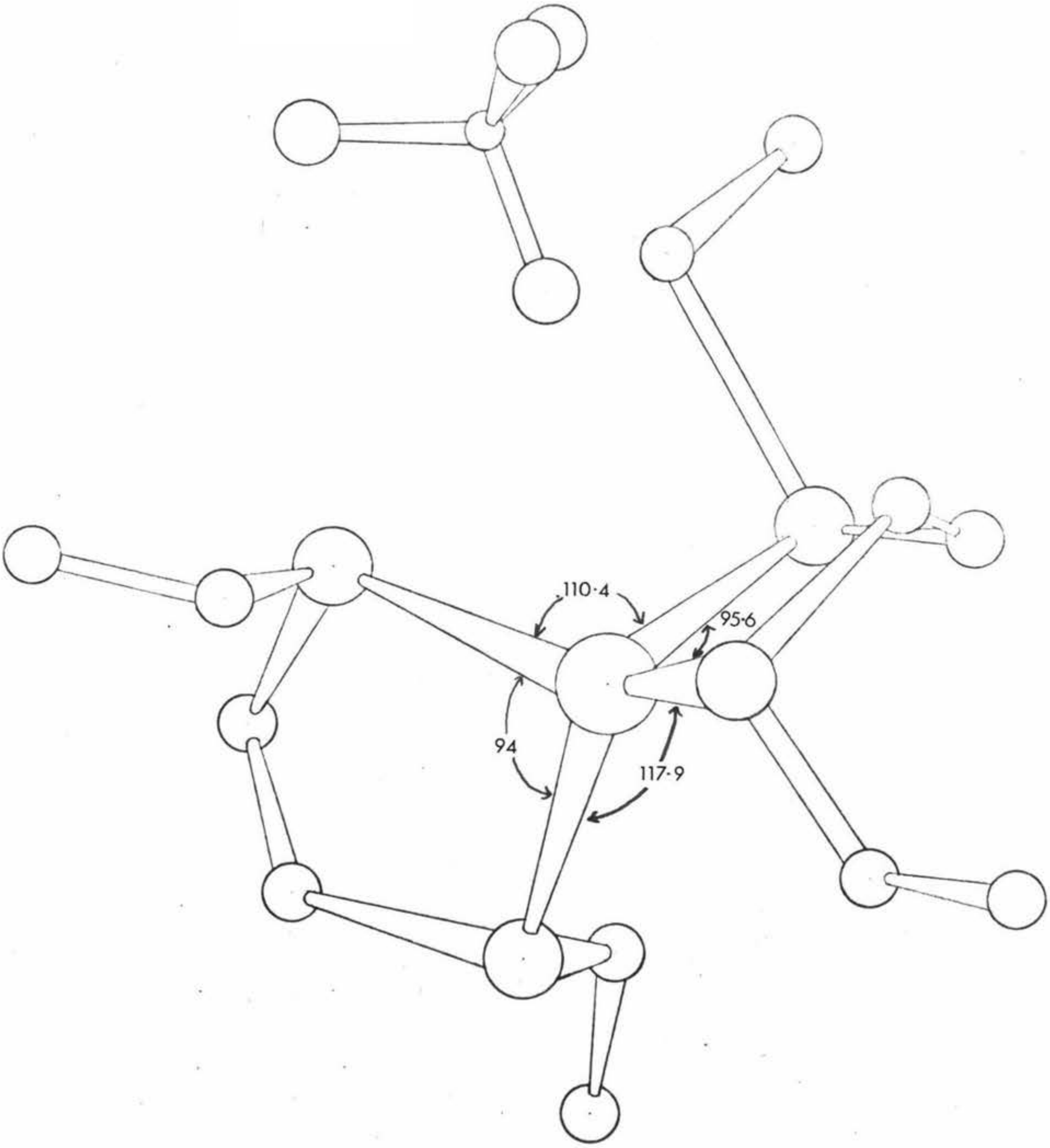


Figure 3.1b Infra-red Spectra

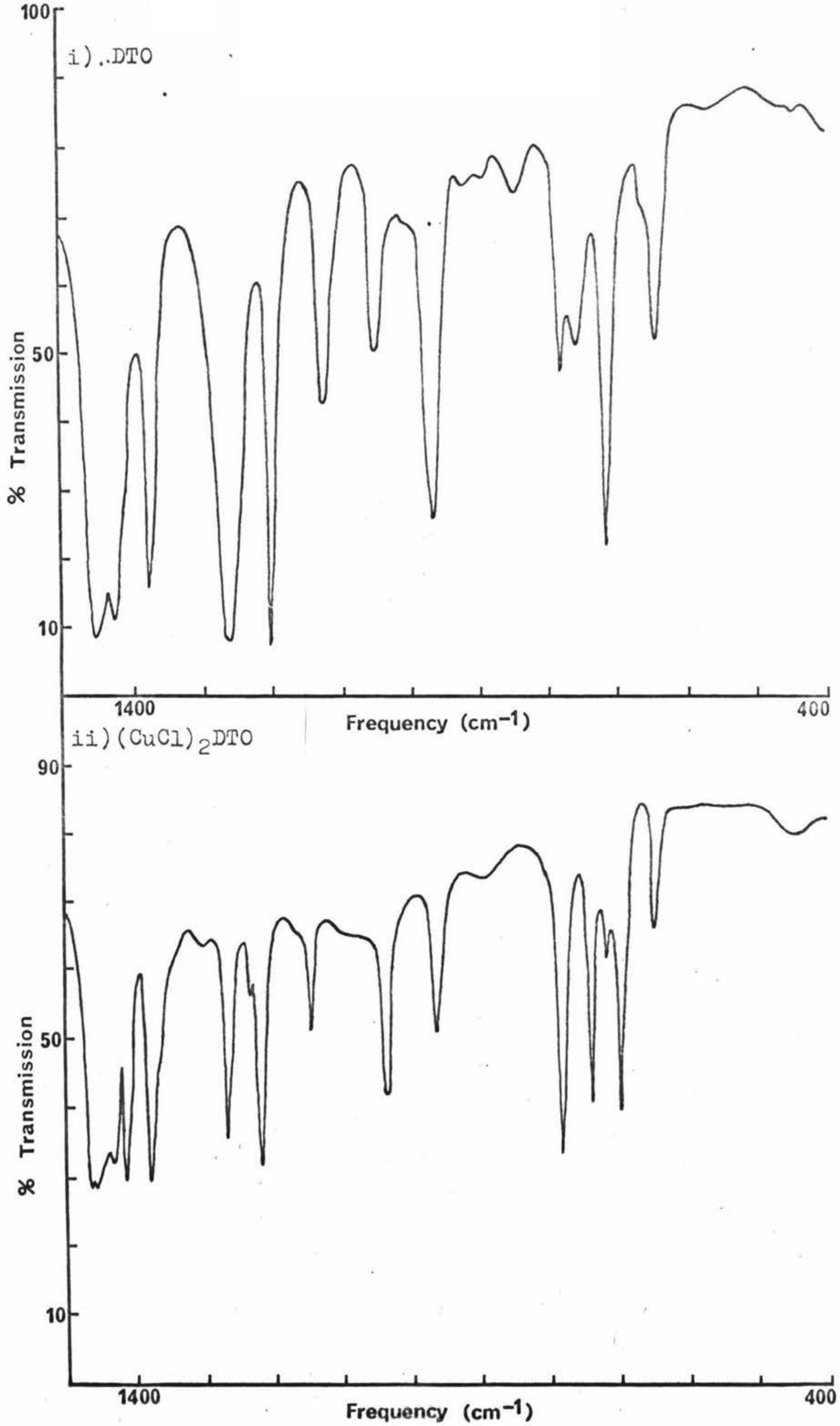
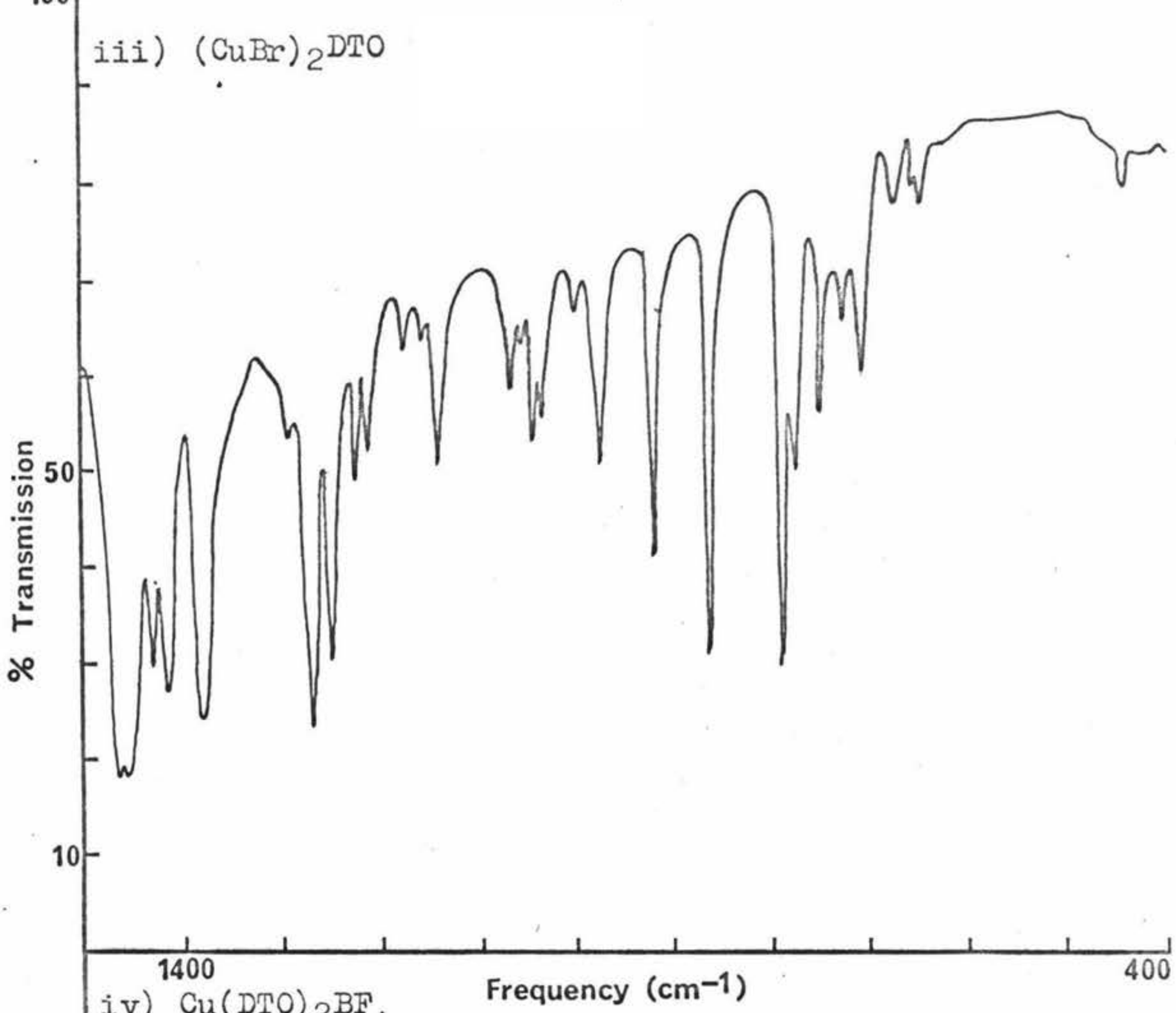
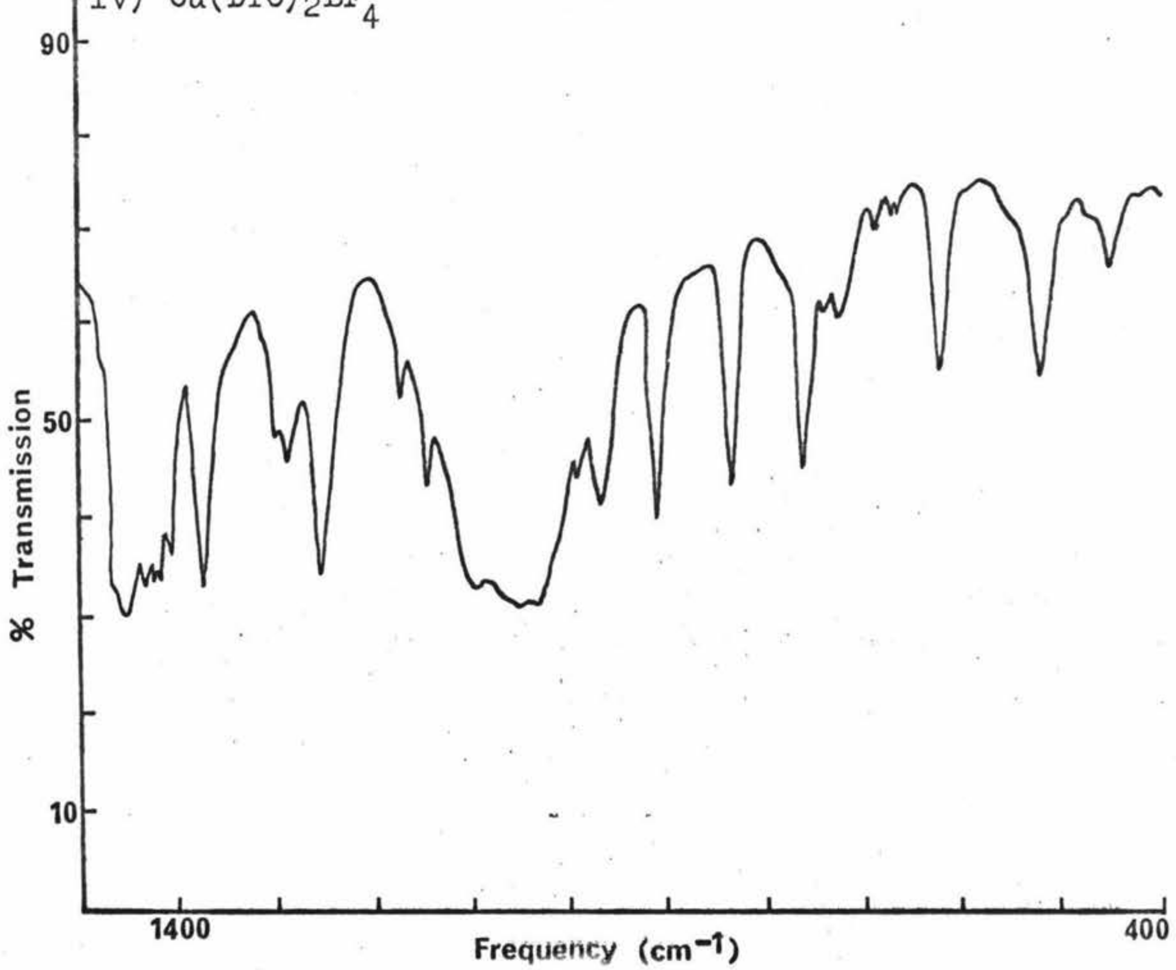


Figure 3.1b Infra-red Spectra continued



iii) $(CuBr)_2DTO$



iv) $Cu(DTO)_2BF_4$

A similar argument can be put forward for the dithiaoctane and dithiahexane complexes. The infra-red spectrum of $(CuCl)_2DTO$ is much simpler than that of the complex. $Cu(DTO)_2BF_4$ where the ligand is chelated in the gauche form and, therefore, the DTO ligand is bridging the two copper atoms in a trans form. Clark and Errington [16] have assigned the infra-red spectrum of the DTO ligand in the solid and liquid states. They say that in the solid state only the trans conformation exists and that in the liquid state there is a mixture of trans and gauche conformations. A comparison of the solid state free ligand and the complex $(CuCl)_2DTO$ can be made using Table 3.1a. On comparison of the infra-red spectra it would appear that all the copper(I) dithiahexane and dithiaoctane complexes with the one exception above would have chelating ligands.

The far infra-red spectra were recorded and the peak positions and possible assignments given in Table 3.1b for copper-halide stretches.

On the basis of known structures, far infra-red and infra-red spectra possible structural types are postulated for each compound. Many structural types are known for copper(I) halide complexes but unfortunately only a few correlated copper-halide stretching frequencies are known, see Table 3.1c and figures 3.1c-l. As a result single crystal x-ray analyses would be necessary to get further information on the copper(I) complexes studied in this work.

From Table 3.1c and Table 3.1d the types of Cu-Cl vibrations can be reasonably well defined with, however,

Table 3.1a. Absorptions of Trans 3,6-dithiaoctane and the complex dichloro(3,6-dithiaoctane) dicopper(I) and their Assignments.

Assignments[a]	Solid DTO	$(CuCl)_2DTO$
	1455s	1461vs,d
	1448s	
	1440s	1438vs,d
	1418s	1415vs
CH_3 symband	1374m	1382vs
		1370m,sh
CH_2 wag	1264s	1268vs
CH_2 wag(gauche)	n.o. ‡	n.o. ‡
	1239m	1237m,sh
CH_2 wag(trans)	1209s	1220s
	1145s	1150m
CH_2 twist(trans)	1053m	1041s
	1025w	
CH_3 rock	n.o. +	973m–s
	892m	895vw,b
CH_2 rock(gauche)	n.o. !	n.o. !
	784m	786vs
	739m	745s
	721m	722w
	671m	705s
C–S str	654w	656m

a=Assignments according to Clark and Errington[16]
vs=very strong
s= strong
m= medium
w= weak
vw= very weak
sh= shoulder
d= doublet
b= broad

n.o.= not observed
\+ a strong peak at 973 is observed in liquid DTO
! a weak band is observed in the liquid DTO and is observed at 853 cm⁻¹. This band is strong in the range 860–837 cm⁻¹ in all the other copper(I) dithiaoctane complexes.
‡ a strong band is observed in the liquid ligand at 1256 cm⁻¹ and is also strong in all the other copper(I) dithiaoctane complexes in the range 1247–1256 cm⁻¹.

Table 3.1b. Far Infra-red Adsorptions of the Copper(I) Halide Complexes.

Compound	ν(Cu-X)[a]	Other Bands
$(CuCl)_2DTO$	218s,br; 181s,br	243w; 235m; 153w; 115w; 98s; 54m
$(CuBr)_2DTO$	152s; 145s,sh	173m,sh; 135m,sh; 121w; 83w; 55w
Cu(DTO)I	159s,sh; 155s	173m,sh; 137m,sh; 97m-s; 49m
Cu(DTH)Cl	271s	285w,sh; 245w; 223w; 200w; 139w; 104w; 88m-s; 72m; 59w-m
Cu(DTH)Br	169s, 152s	202m; 180m,br; 115s; 71m; 64m,sh; 47m
Cu(DTH)I	139(?)m,br +	183w,br; 98s; 87s,sh; 79s,br; 63m; 53w

a ν(Cu-X) frequencies in cm^{-1}
\+ This band may have other contributions from C-C-S deformation in the ligand.

s= strong
m= medium
w= weak
sh= shoulder
br= broad

Table 3.1c <u>Copper-Halide Frequencies and Correlated Structures.</u>

Compound	ν(Cu-Cl)	Ref (i.r.)	Structure Type	Ref (struct)
$[Cu(TMDPDS)Cl]_2$	257	this work	Terminal Cl Fig 3.1c	58
$(CuCl)_2(DPE)_3$	244	45	Terminal Cl Fig 3.1d	59
$[Cu(TMPS)Cl]_3$	275 299	56 49	Terminal Cl Fig 3.1e	60
$Cu(bdtm)Cl.(CH_3)_2CO$	279	57	Terminal Cl Fig 3.1f	57
$[Cu(1,5\text{-}cod)Cl]_2$	227	50	Bridging Cl Fig 3.1g	61
$[Cu(C_8H_8)Cl]_2$	254,222	50	Bridging Cl Fig 3.1h	62
$[Cu(C_7H_8)Cl]_4$	238	50	Cubane Fig 3.1i	63
$[Cu(AsEt_3)I]_4$	131,137	54	Cubane Fig 3.1j	64
$[Cu_3Cl_2(DPM)_3]^+ Cl^-$	287-236	45	Fig 3.1l	46
$[Cu(nas)I]_2$	175,128	53	Bridging I	65

Table 3.1d Copper-Halide Stretching Frequencies Without Correlated Structures

Compound	Cu-X (cm^{-1})	Reference	Comment
$Cu(nas)Br$	202,145	53	Band pattern similar to that of the iodine analogue of which the structure is known. Halogen atoms bridging.
$Cu(nas)Cl$	232,162	53	
$(CuCl)_2(DPPA)_3$	267	52	Agrees with a tetrahedral C_{3v} configuration of 3P and 1X around each copper atom where a single $\nu(CuX)(A_1)$ mode is expected.Therefore terminal Cu-X
$(CuBr)_2(DPPA)_3$	202	52	
$Cu(PCy_3)_2Cl$	255	68	Osmometric studies show compound to be monomeric in benzene.PCy group is too bulky for a third PCy group to be coordinated[a].Therefore,the copper atom is trigonal planar and Cu-X is terminal.
$Cu(\phi_2Te)_3Cl$	265	51	Copper does not have a coordination number greater than four.Therefore, Cu-Cl is terminal.
$[Cu(R_2Te)_2Cl]_2$		51	Powder photographs show chlorides and bromides to be isostructural. All other bands are common. Therefore,bridging halide atoms.
R = p-toloyl	183,117		
R = p-EtO-ϕ	185,128		
$[Cu(R_2Te)_2Br]_2$			
R = p-toloyl	164,92		
R = p-EtO-ϕ	163,100		
$Cu(R_2Te)_2I$ R = p-toloyl	163	51	On the basis of other assignments this is too high for bridging iodine and therefore $\nu(Cu-I)$ is terminal.
$Cu(DTH)(\phi_3P)Cl$	245	This work	$\nu(Cu-Cl)$ is terminal due to copper(I) not able to have coordination greater than four and that DTH is chelating.

Key for Tables 3.1c and 3.1d

TMDPDS=tetramethyldiphosphinedisulphide

DPE =1,2-bis(diphenylphosphino)ethane

TMPS =trimethylphosphine sulphide

bdtm =bis(diphenylphosphinothioyl)methane

1,5-cod=1,5-cyclooctadiene

DPM =bis(diphenylphosphino)methane

C_8H_8 =cyclooctatetraene

nas =o-dimethylaminophenyldimethylarsine

C_7H_8 =norbornadiene

$AsEt_3$ =triethylarsine

DPPA =bis(diphenylphosphino)acetylene

PCy_3 =tricyclohexylphosphine

Ø$_2$Te =diphenyltelluride

(p-tolyl)$_2$Te=di(p-methylphenyl)telluride

(p-EtOØ)$_2$Te=di(p-ethoxyphenyl)telluride

DTH =2,5-dithiahexane

Ø$_3$P =triphenylphosphine

a =The crystal structure of $Cu(Cy_3)P_2ClO_4$ has been determined and shows that the copper atom is trigonal planar. The structure confirms Moers statement that the PCy_3 group is too bulky to allow a fourth ligand to coordinate to the copper atom.

Figure 3.1c Perspective View of $[Cu(TMDPDS)Cl]_2$ [58]

Where TMDPDS=tetramethyldiphosphinedisulphide.

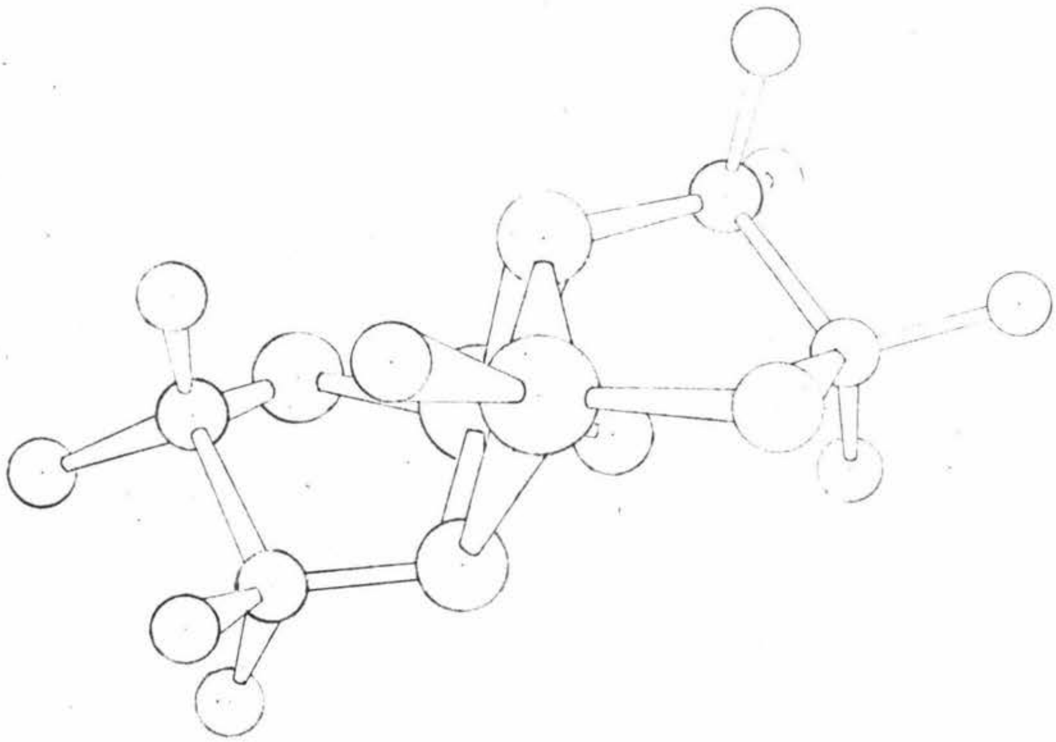


Figure 3.1d Perspective View of $(CuCl)_2(DPE)_3$ [59]

Where DPE=bis(diphenylphosphine)ethane

Phenyl rings have been ommitted for clarity.

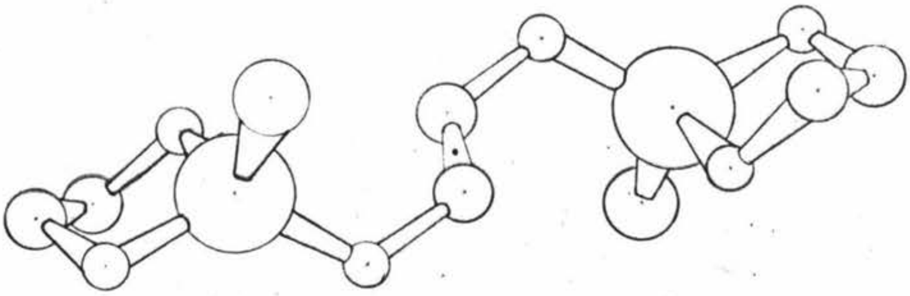
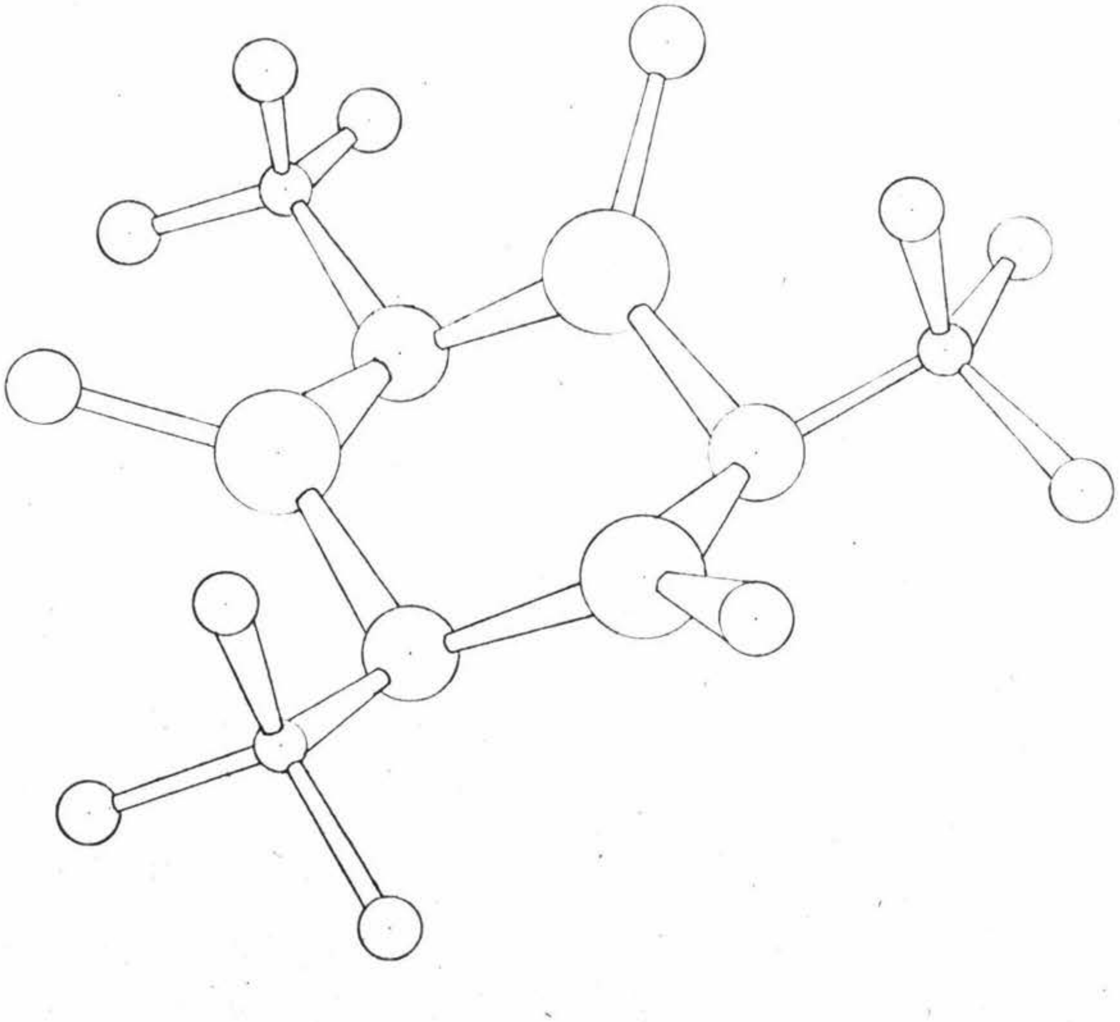


Figure 3.1e Perspective View of [Cu(TMPS)Cl]$_3$ [60]
Where TMPS=trimethylphosphinesulphide



some areas of overlap. Terminal ν(Cu–Cl) range from as high as 299cm^{-1} [49] to as low as 244cm^{-1} [45]. The ν(Cu–Cl) stretching frequencies in structures where the chlorine atom bridges two copper atoms usually have two adsorptions although often only one is seen. The assigned range is from as high as 254cm^{-1} [50] to as low as 117cm^{-1} [51]. The ν(Cu–Cl) stretching frequencies in structures where the chlorine bridges three copper atoms occur at 238cm^{-1} [50] but also a broad band at 287–236cm^{-1} [45]. The terminal ν(Cu–Br) stretching frequency occurs at 202cm^{-1} [52], while where the bromine is bridging two copper atoms the ν(Cu–Br) stretching frequencies again usually occur as two bands with one as high as that of a terminal Cu–Br and one much lower [53] or two bands both below 200cm^{-1} [51]. There have been no accurate determinations of ν(Cu–Br) where the bromine atom is bridging three copper atoms. Terminal ν(Cu–I) stretching frequencies have not been characterised.[49] In $[Cu(TMPS)I]_n$, where TMPS is trimethylphosphinesulphide, Nakamoto [49] assigned a band at 164cm^{-1} to be that of ν(Cu–I) stretch but did not commit himself to say whether it was terminal or bridging. Volponi et al [53] assigned ν(Cu–I), where the iodine atom bridges two copper atoms, at 175cm^{-1} and 128cm^{-1}. In structures where the iodine atom bridges three copper atoms, the ν(Cu–I) vibrations appear in the range 131–143cm^{-1}.[54] McWhinnie [51] says that 163cm^{-1} for ν(Cu–I) is too high for bridging iodine because it is the same as bridging bromine and would, therefore, have to be terminal. He also says that strong bands at 161cm^{-1} and 111cm^{-1} for $(R_2Te)CuI$ are that of bridging ν(Cu–I). If that is the case then 163cm^{-1} for ν(Cu–I) must be near the lower extreme for terminal.

The far infra–red spectrum for (CuCl)$_2$DTO gives two broad bands with centres at 218cm^{-1} and 181cm^{-1}. As the range for terminal ν(Cu–Cl) stretch is 244cm^{-1}–299cm^{-1} on available data it appears that the frequencies of 218cm^{-1} and 181cm^{-1} can be assigned to those of bridging ν(Cu–Cl). With the metal:ligand ratio of 2:1 and the ligand bridging there are six possible structures: (a) the cubane type as in figure 3.1j, (b) the polymeric double bridge structure as in figure 3.1k, (c) the step conformation as in figure 3.1m, (d) the polymeric step structure as in figure 3.1o, and (e) the polymeric chain similar to figure 3.1h, and (f) two polymeric step structures bridged by DTO as figure 3.1p.

I will now consider each structural type.

(a) The cubane type in figure 3.1j has a Cu....Cu distance range of 3.118A$^\circ$ to 3.430A$^\circ$ in the structure of (CuClϕ_3P)$_4$ In the Cu(DTO)$_2$BF$_4$ complex it is shown that 3,6–dithiaoctane has a 'bite' of 3.406A$^\circ$ and 3.377A$^\circ$ [27] .However, DPM, (bis(diphenylphosphino)methane) has a 'bite' of 3.1A$^\circ$ and in all complexes of the type (CuX)$_2$DPM, where X=Cl, Br, or I, it has been shown by single crystal x–ray structure [46,55] that the complexes have a step configuration as in figure 3.1m. On this basis it seems unlikely that the cubane structure would persist with (CuCl)$_2$DTO.

(b) The polymeric double bridge structure of figure 3.1k is a fairly loose structure and therefore, could be preferred. Also a long and a short Cu–Cl bond would give different

Figure 3.1f Perspective View of Cu(dptm)Cl [57]
Where dptm=bis(diphenylphosphinothioyl)methane

Only the first Carbon atoms of the phenyl rings are shown.

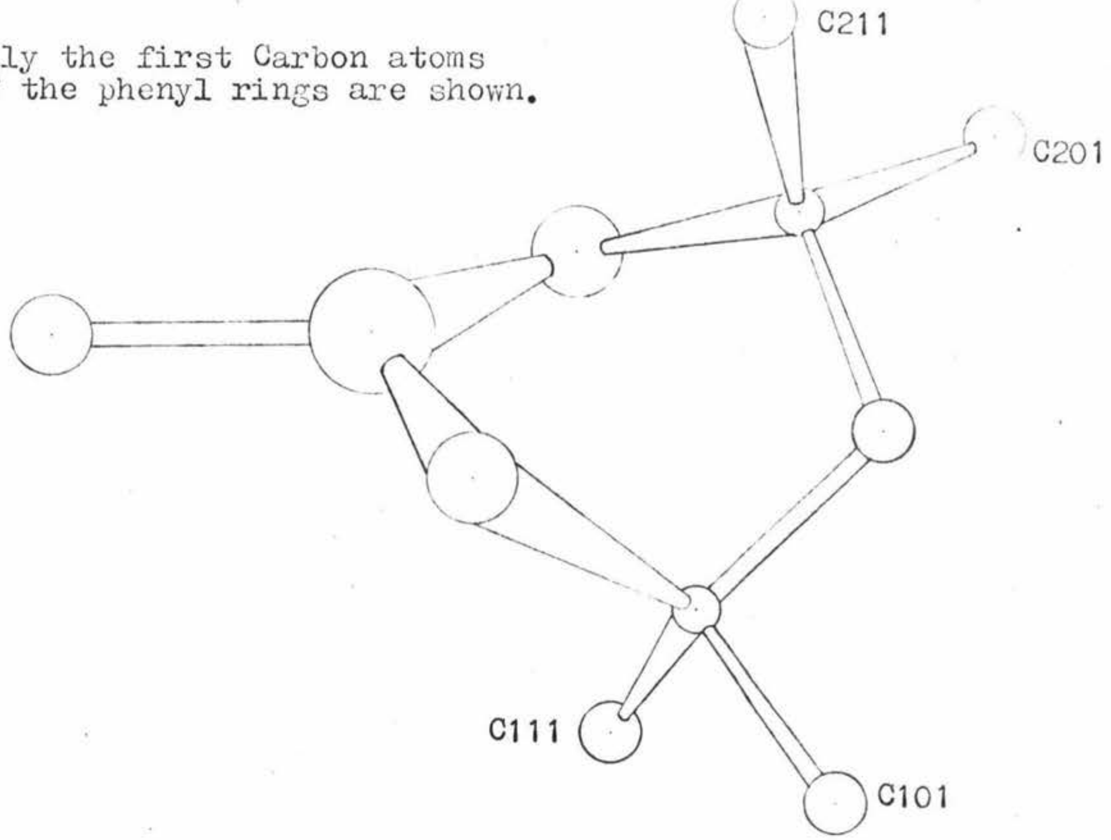


Figure 3.1g Perspective View of $[Cu(1,5cod)Cl]_2$ [61]

Where 1,5cod=1,5-cyclooctadiene

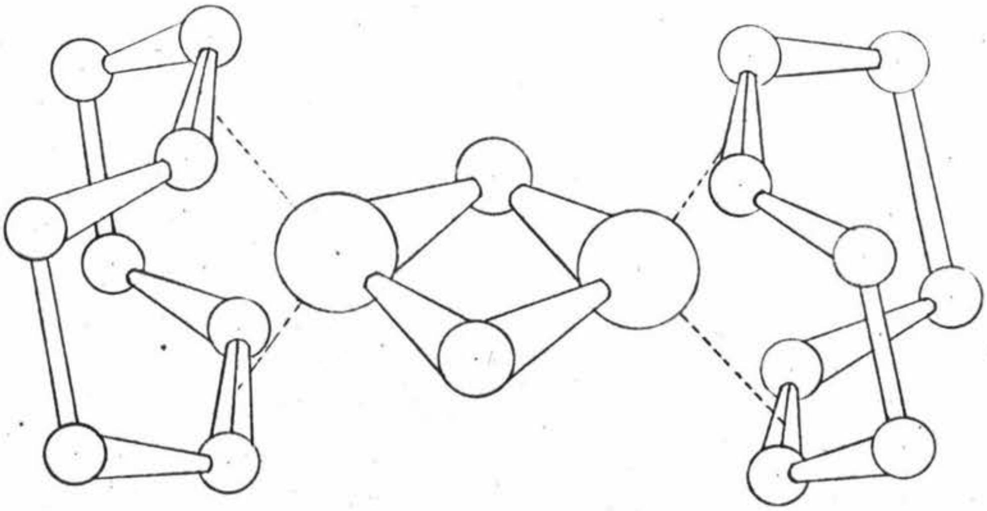


Figure 3.1h Perspective View of $[Cu(C_8H_8)Cl]_n$ 62
Where C_8H_8=cyclooctatetraene.

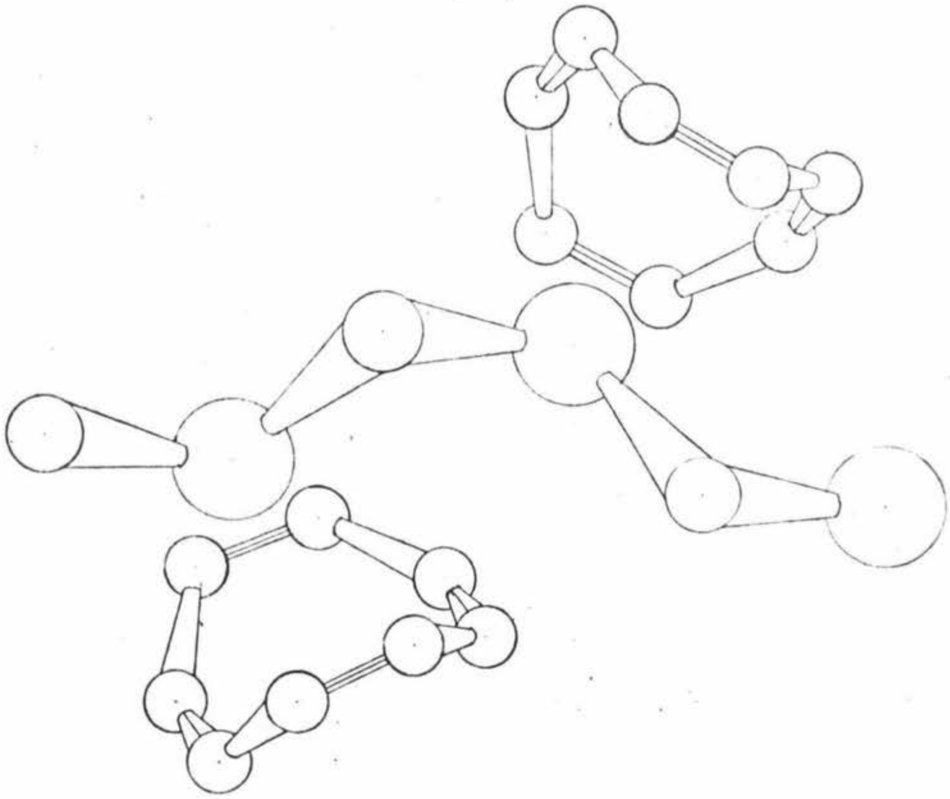


Figure 3.1i Perspective View of $[Cu(C_7H_8)Cl]_4$ 63
Where C_7H_8=norbornadiene

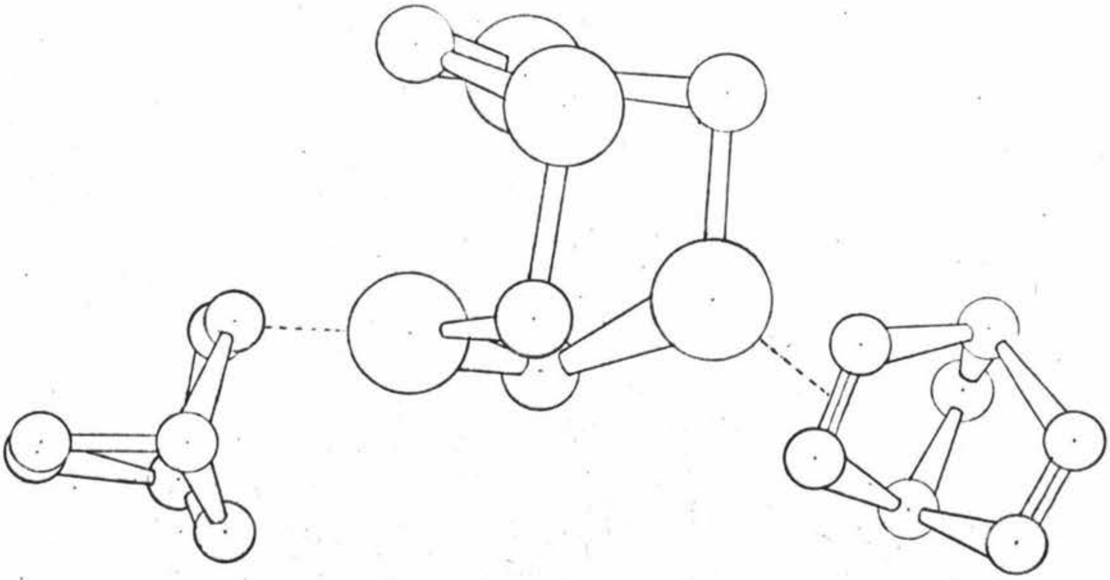


Figure 3.1j Perspective View of $[Cu(AsEt_3)I]_4$ [64]
The ethyl groups have been omitted for clarity.

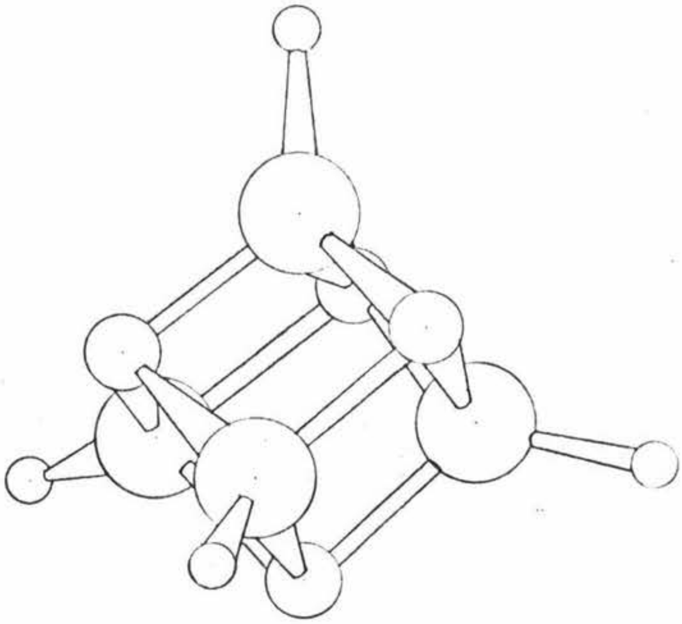


Figure 3.1k The polymeric doubly bridged chain of $(CuClEt_4P_2)_n$ [46]
Only the first Carbon atom of each ethyl group is shown.

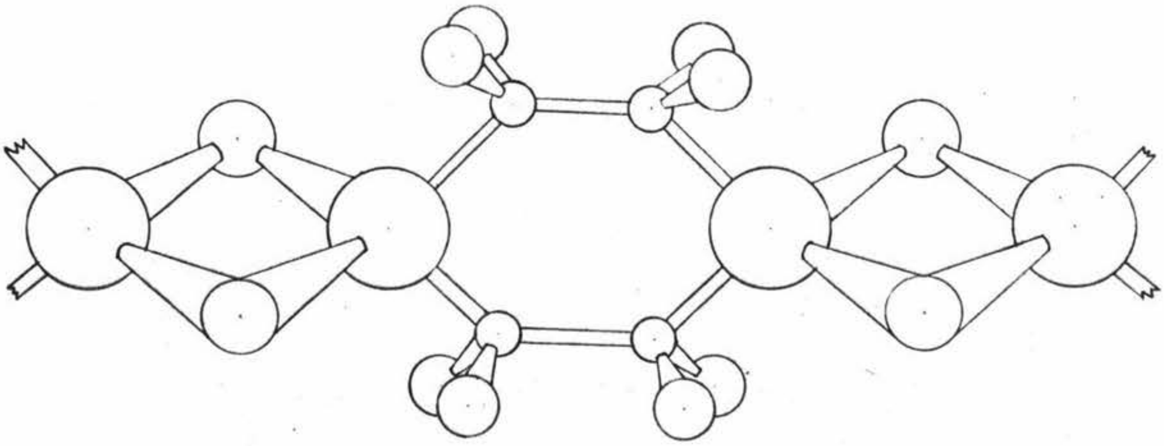


Figure 3.11 $[Cu_3Cl_2DPM_3]^+ Cl^-$ [46]

Where DPM=bis(diphenylphosphino)methane

The phenyl rings and the third DPM molecule have been omitted for clarity.

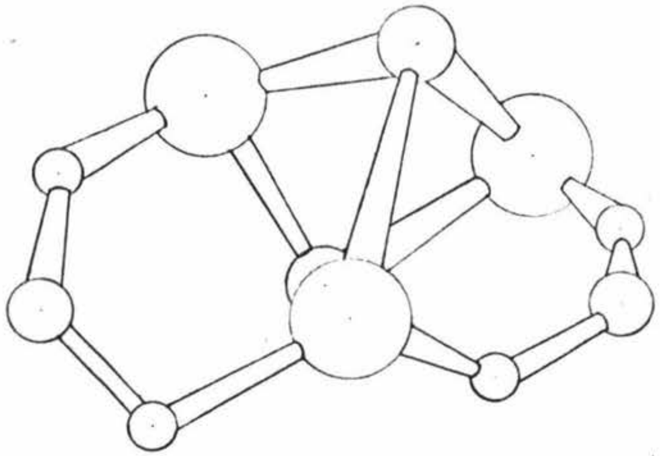


Figure 3.1m $[(CuCl)_2DPM]_2$ [55]

Where DPM=bis(diphenylphosphino)methane

The phenyl rings have been omitted.

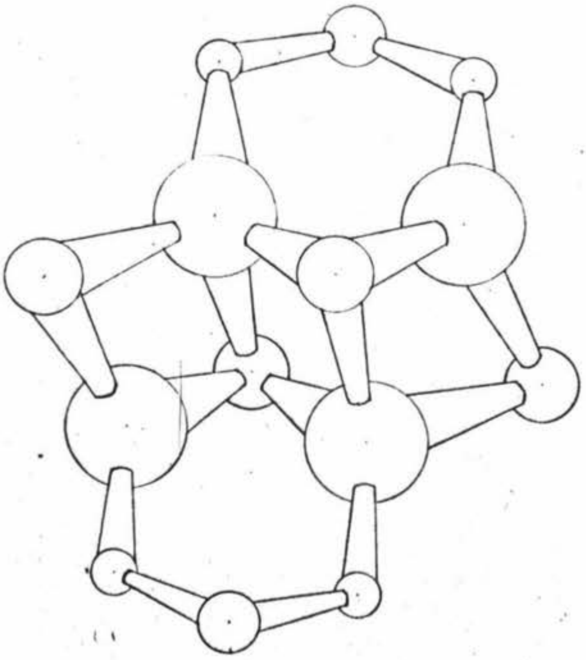


Figure 3.1n Perspective View of $(CuClEt_2S_2)_n$ [66]

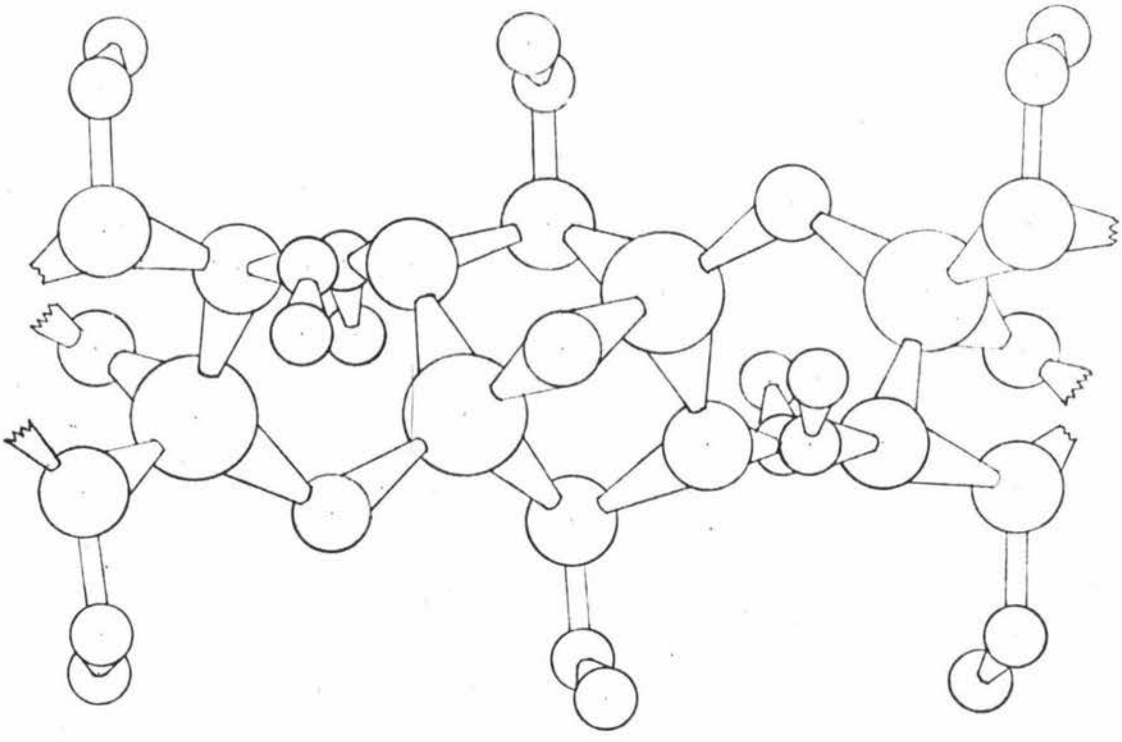


Figure 3.1o Polymeric Step Structure D=a donor atom [46]

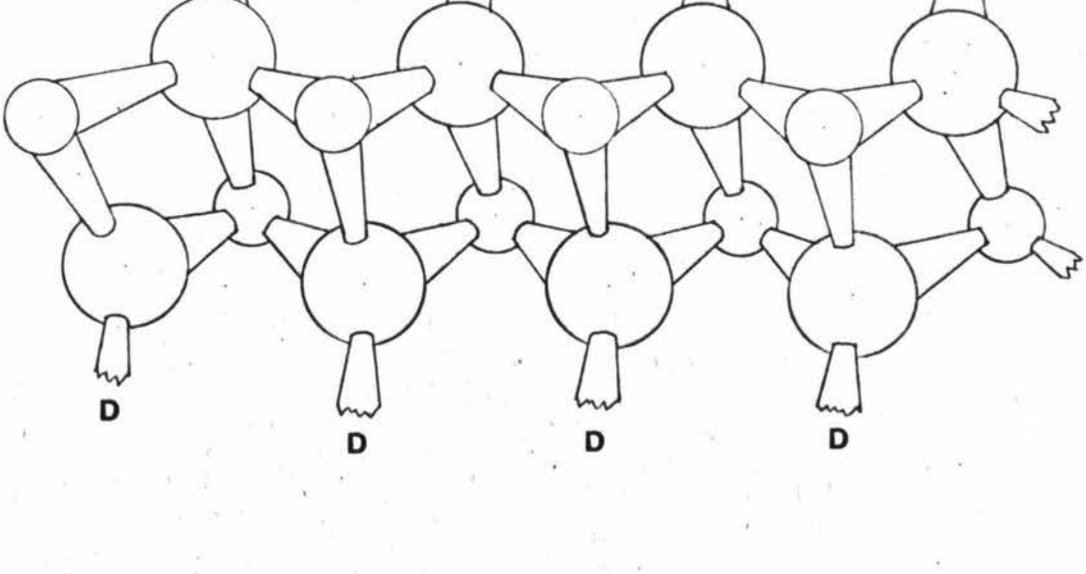
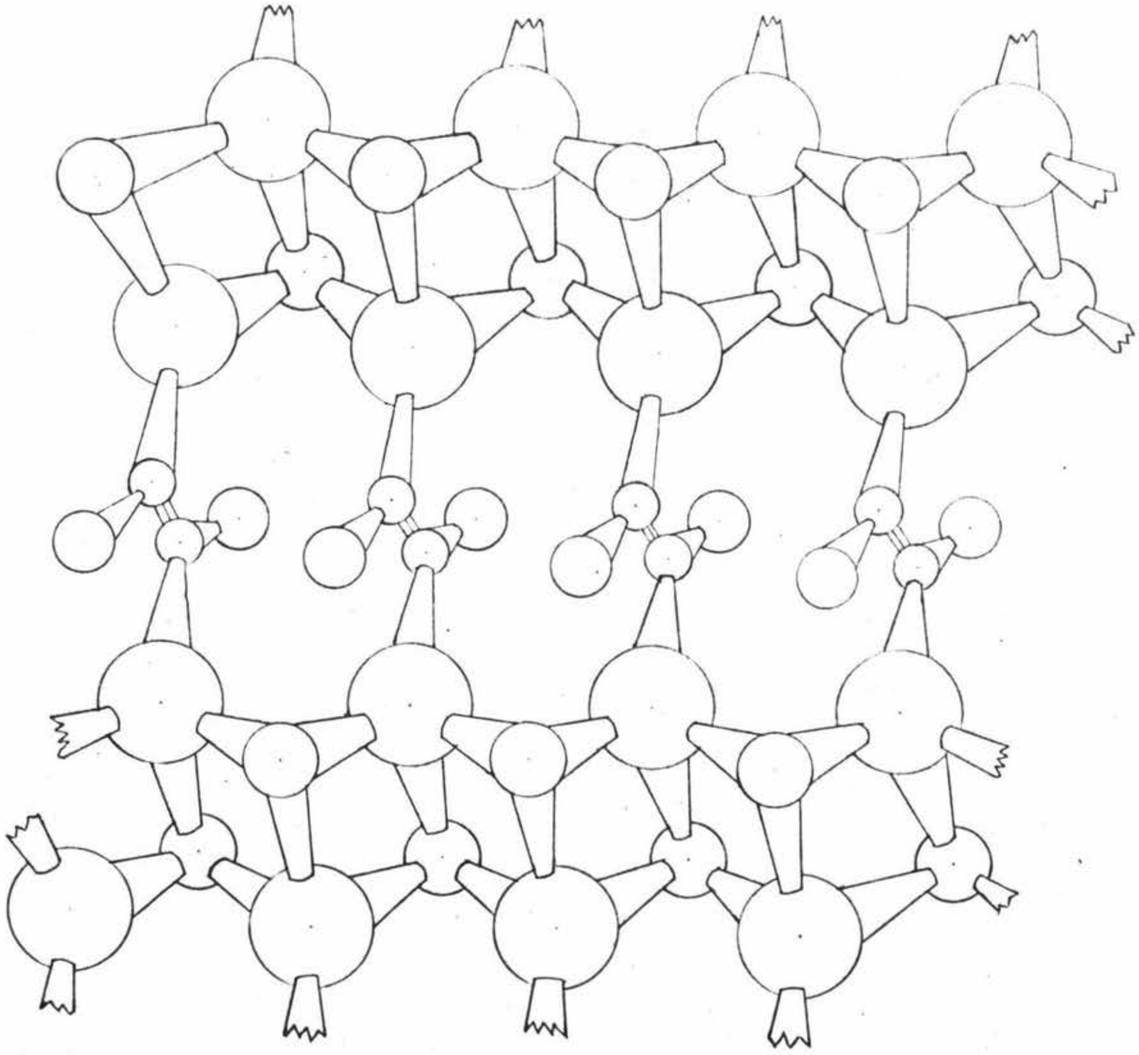


Figure 3.1p Perspective View of $(CuClN_2Me_2)_n$ 67
Where N_2Me_2=azomethane



stretching frequencies with the long bond lower in frequency than that of the shorter Cu–Cl bond.

(c) The step configuration in figure 3.1m is again consistent with the infra-red data to hand. There are two types of chlorine atoms; one bridging two copper atoms and one bridging three copper atoms. It would, therefore, be expected that the ν(Cu–Cl) for the trigonal chlorine would be lower than that for the doubly bridging chlorine. This is consistent with infra-red data as the 218cm^{-1} band is consistent with doubly bridging chlorine.

(d) The polymeric step structure of figure 3.1o has only one type of chlorine atom; a triply bridging chlorine that one might expect to have a lower infra-red stretching frequency than those assigned.

(e) A polymeric chain of the type shown in figure 3.1h but with one donor atom from a ligand is known for phosphine and for the complex $[Cu(C_8H_8)Cl]_n$ where C_8H_8 is cyclooctatetraene,[62] giving a trigonal planar copper atom. The ν(Cu–Cl) stretching frequencies for the cyclooctatetraene complex [50] were higher than those assigned here.

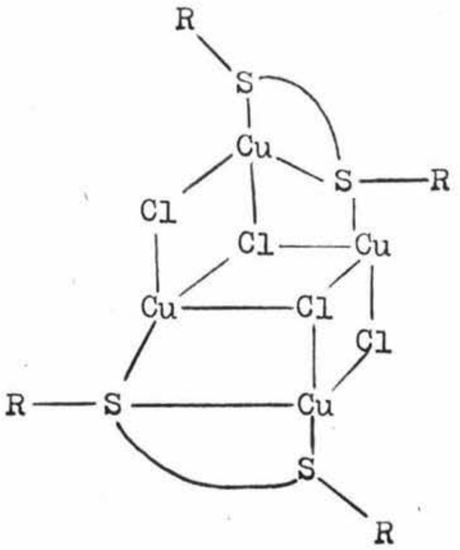
(f) Two polymeric step structures bridged by a bidentate ligand as in figure 3.1p would enable the ligand to be fully in the trans conformation about the central C–C bond.

In the structural types of (b) and (f) the ligands are special in that the donor atoms are next to each other which is energetically favourable to trans conformations. Hence one could say that the ligands are designed to bridge in the manner shown. If the two donor atoms are separated by one or more carbon atoms, as in DPM, then it appears that these two structures are not preferred. On this basis structures (c), (d) and (e) may be preferred for the complex $(CuCl)_2DTO$.

Dibromo(3,6-dithiaoctane)dicopper(I), $(CuBr)_2DTO$ has an infra-red spectrum indicating a chelating DTO ligand. The far infra-red spectrum has two strong bands 152cm^{-1}s and 145cm^{-1}s, sh. On the basis of other assignments it would appear that these are bridging bromine stretches, and that the Cu-Br bond strengths are similar. A monomeric structure seems unlikely as this would involve an angular two coordinate copper atom which is rather exposed. A polymeric type structure would be more favourable for this compound. Some of these polymeric structures may contain sulphur atoms bridging two copper atoms as well as the ligand being chelated. For an example of a simple structure with this type of bonding see figure 3.1q.

Iodo(3,6-dithiaoctane)copper(I), Cu(DTO)I, has an infra-red spectrum indicating a chelating ligand. The far infra-red spectrum has two very strong bands at 155cm^{-1} and 159cm^{-1} (shoulder). A doublet indicates that the iodine atom is bridging but splitting due to some other factor can not be ruled out as these bands seem to be as high as bridging bromine stretches, and could therefore, be assigned to a terminal ν(Cu-I). If the ν(Cu-I) is terminal then a trigonal planar arrangement about the copper atom as in figure 3.1f would be a valid prediction. If the ν(Cu-I) stretch is one of a bridging iodine then a high symmetry about the

Figure 3.1q



copper atom would be expected. A cubane type structure as in figure 3.1j is unlikely as a five coordinate copper(I) atom is unfavourable and the ν(Cu–I) is inconsistent with those measured by Knappstein for $[Cu(AsR_3)I]_4$ where $R=CH_3, CH_3CH_2$, or C_6H_5 who assigned doublets in the range 131 cm⁻¹ to 143 cm⁻¹.[54]

Thiocyanato(3,6-dithiaoctane)copper(I), Cu(DTO)SCN, contains a chelating ligand according to the infra-red spectrum. For the thiocyanate anion a strong ν(C≡N) stretch was observed in the infra-red spectrum at 2110 cm⁻¹ and at 2102 cm⁻¹ in the Raman spectrum; the ν(C–S) stretch could not be identified in the infra-red because of ligand bands but was assigned as a medium-strong band at 776 cm⁻¹ in the Raman spectrum; the δ(SCN) band was easily identified as two medium bands at $472 cm^{-1}$ and $460 cm^{-1}$ in the infra-red spectrum. Cox and Howatson [69] assigned doublets in the range $441 cm^{-1}$ to $456 cm^{-1}$ for δ(SCN) in the silver complexes AgSCNL where $L = PEt_2Ø$, $P(n-Bu)_3$, PMe_3, and single bands in the range $462 cm^{-1}$ to $494 cm^{-1}$ for $AgSCNL_2$ where $L = Ø_3P$, Cy_3P, $Ø_3Sb$, $ØEt_2P$, $Ø_3As$. Nathan has given a table relating the positions of thiocyanate bands as a function of bonding (see Table 3.1e).

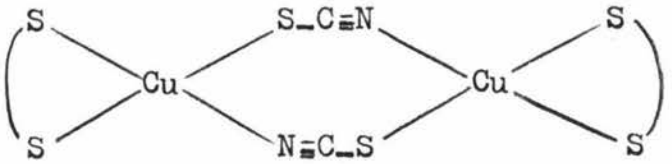
Table 3.1e Positions of Thiocyanate Bands as a Function of Bonding Mode.

Bonding Mode	C≡N Stretch (cm^{-1})	C–S Stretch (cm^{-1})	NCS Bend (cm^{-1})
Ionic	2050–2070	743–749	470–485
N-bonded	2040–2080	780–860	450–490
S-bonded	2080–2120	690–720	400–440
SCN Bridge	2150–2170	760–780	450

Taken from L.C.Nathan J.Chem Ed 51, 285, (1974)

From this set of data the ν(C≡N) indicates that the thiocyanate group is s bonded, the ν(C–S) indicates a bridging thiocyanate, and the δ(NCS) indicates that the thiocyanate is N bonded. This is also consistent with data obtained by Cox and Howatson for the silver(I) complexes AgLSCN and AgL_2SCN. Pecile [70] suggests that in the solid state studies the ν(C–S) gives the more reliable type of thiocyanate bonding. If this is so then it would appear that the thiocyanate group is bridging possibly giving a dimeric structure as in figure 3.1r. The complex $\mathrm{AgSCN(\varnothing_3P)_2}$ has a dimeric structure involving a central $\mathrm{(AgSCN)_2}$ ring [71] whereas the complex $\mathrm{AgSCN(n\text{-}Pr)_3P}$ contains zigzag polymeric -Ag-SCN-Ag-SCN- chains cross-linked in pairs by Ag-S bonds to form double chains having a stair-step configuration.[72] As DTO is bidentate a structure similar to that for $\mathrm{AgSCN(\varnothing_3P)_2}$ is more likely than that for the complex $\mathrm{AgSCN(n\text{-}Pr)_3P}$. The crystal structure of $\mathrm{[\varnothing_2(CH_3)PCu(NCS)]_2}$ [73] shows a dimeric structure with bridging thiocyanates.

Figure 3.1r Possible Dimeric Structure for Cu(DTO)SCN



Bis(3,6-dithiaoctane)copper(I)tetrafluoroborate, $\mathrm{Cu(DTO)_2BF_4}$, as mentioned earlier, has been determined structurally by single crystal x-ray analysis. The copper atom has a distorted tetrahedral geometry with S-Cu-S bond angles shown in figure 3.1a. There is some π bonding between the copper and sulphur atoms as the covalent radii give a theoretical Cu-S bond distance of 2.39Å and the actual bond distances are in the range 2.279Å to 2.318Å.

Chloro(2,5-dithiahexane)copper(I), Cu(DTH)Cl, has a strong ν(Cu-Cl) stretch at 271 $\mathrm{cm^{-1}}$ which appears to be that of a terminal ν(Cu-Cl). It seems that the copper atom would have a trigonal planar symmetry as in figure 3.1f.

Bromo(2,5-dithiahexane)copper(I), Cu(DTH)Br, has two strong bonds at 169cm^{-1} and 152cm^{-1} indicating that the bromine atoms are bridging. The simplest possible structure may be similar to that in figure 3.1q with the bromine atoms bridging between the two copper atoms.

Iodo(2,5-dithiahexane)copper(I), Cu(DTH)I gave a poor far infra-red spectrum with a broad band at 139cm^{-1} which may be assigned to ν(Cu-I). However as this assignment is very tentative no comment on structure can be made.

3.2 EXPERIMENTAL

For a description of the solvents and ligands see Chapter 2.4.

$LiI.H_2O$ and KSCN were laboratory reagent grade supplied by B.D.H. Ltd.

For the reactions all solvent volumes were kept to a minimum.

SYNTHESES

[Dichloro(3,6-dithiaoctane)dicopper(I)]$_n$ $[(CuCl)_2DTO]_n$

170mg (1.0mmoles) $CuCl_2.2H_2O$ were dissolved in methanol and 150mg (1.0 mmoles) DTO added to form a dark green solution. This was well stirred and heated while hypophosphorous acid (H_3PO_2) was added dropwise until the solution went clear. The clear solution had 3 more drops of H_3PO_2 added to it and was then allowed to cool. On standing overnight white crystals formed which were filtered off, washed with dry diethyl ether, and dried under vacuum. The yield was 68%, and the m.p. 128-9° C. Analytical results for $Cu_2Cl_2\ C_6H_{14}S_2$: calculated %C=20.69, %H=4.05, %Cl=20.36 observed %C=20.29, %H=4.42, %Cl=21.10.

[Dibromo(3,6-dithiaoctane)dicopper(I)]$_n$ $[(CuBr)_2DTO]_n$

407mg (1.8mmoles) $CuBr_2$ were dissolved in methanol and 200mg (1.3mmoles) DTO added to give a dark brown solution. This was well stirred and heated while hypophosphorous acid was added dropwise until the solution went clear and a white precipitate formed. The white precipitate was filtered off, washed with dry diethyl ether, and dried under vacuum. The yield was 80%, and the m.p. 84.5-86°C(decomposition). Analytical results for $Cu_2Br_2C_6H_{14}S_2$: calculated %C=16.48, %H=3.23, %Br=36.56; observed %C=16.39, %H=3.47, %Br=37.11.

Iodo(3,6-dithiaoctane)copper(I)   Cu(DTO)I

170mg (1.0mmoles) $CuCl_2.2H_2O$ were dissolved in methanol and 150mg (1.0mmoles) DTO added slowly to give a dark green solution. 303mg (2.0mmoles) $LiI.H_2O$ in a methanol solution was added to give a dark red-brown solution and a creamy-yellow precipitate. The precipitate was filtered off, washed with dry diethyl ether, and dried under vacuum. The yield was 66%, and at 125°C the compound went brown suggesting decomposition. Analysis for $CuIC_6H_{14}S_2$: calculated %C=21.15, %H=4.14, %S=18.80; observed %C=21.04, %H=4.37, %S=18.21.

Thiocyanato(3,6-dithiaoctane)copper(I)   Cu(DTO)SCN

242mg (1.0mmoles) $Cu(NO_3)_2.3H_2O$ were dissolved in acetone and 150mg (1.0mmoles) DTO added to give a dark green solution. 195mg (2.0mmoles) KSCN was slowly added as an acetone solution to give a dark red solution and a white precipitate of KNO_3. The white precipitate was filtered off, and the red filtrate treated with a few drops of H_3PO_2 until the solution went clear and then left to stand. White crystals precipitated and these were filtered off after 15 minutes, washed with dry diethyl ether, and dried under vacuum.

The yield was 79% and at 125-126° C the crystals went brown suggesting decomposition. Analytical results for $CuC_7H_{14}S_3N$: calculated %C=30.92, %H=5.19,%S=35.37, %N=5.15; observed %C=31.23, %H=5.55, %S=34.23, %N=5.05.

Bromo(2,5-dithiahexane)copper(I) Cu(DTH)Br

335mg (1.5mmoles) $CuBr_2$(anhydrous) were dissolved in methanol and 183mg (1.5mmoles) DTH added to give a dark brown solution. While stirring and gentle heating H_3PO_2 was added dropwise until the solution turned clear and a white precipitate formed. The precipitate was filtered off, washed with dry diethyl ether and dried under vacuum. The yield was 83% and the m.p. was 128-130° C cf literature value 161-162°C.[14] Analytical results for $CuBrC_4H_{10}S_2$: calculated %C=18.08, %H=3.79, %Br=30.08; observed %C=18.82, %H=3.89, %Br=30.15. The above compound has previously been reported by Bratermann and Wilson,[14] and Bell and Bennett.[43] Both prepared the compound by different methods. Bratermann and Wilson [14] prepared the compound in a way similar to the chloride. Bell and Bennett used an aqueous medium and added DTH to $CuSO_4.6H_2O$ to get an oily compound and then added KBr. The brown solution reduced on standing and shaking.[43]

Bis(3,6-dithiaoctane)copper(I)tetrafluoroborate $Cu(DTO)_2BF_4$

172mg (0.5mmoles) $Cu(BF_4)_2 \cdot 6H_2O$ were dissolved in methanol and 150mg (1.0mmoles) DTO added slowly to give a dark green solution. On the addition of dry diethyl ether the copper(II) complex was reduced and a cloudy white solution resulted. This was left to stand and clear crystals formed overnight. The crystals were filtered off, washed with dry diethyl ether and dried under vacuum. The yield was 21% and the m.p. was 85-6° C. Analytical results for $CuBF_4C_{12}H_{28}S_4$: calculated %C=31.96, %H=6.26; observed %C=32.03, %H=6.31.

Chloro(2,5-dithiahexane)copper(I) Cu(DTH)Cl

170mg (1.0mmoles) $CuCl_2 \cdot 2H_2O$ were dissolved in methanol and 150mg (1.0mmoles) DTH added to give a dark green solution. While stirring and heating H_3PO_2 was added dropwise until the solution turned clear. The solution was allowed to cool overnight to yield the clear crystalline product, which was filtered off, washed with dry diethyl ether, and dried under vacuum. The yield was 92% and at 133-138° C the crystals changed to white and melted at 143° C. Literature value [14] (Bratermann and Wilson) 148-150° C. Analytical results for $CuClC_4H_{10}S_2$: calculated %C=21.72, %H=4.56, %Cl= 16.02; observed %C=22.17, %H=4.88, %Cl=16.42.

Bratermann and Wilson prepared this compound by reacting $CuCl_2 \cdot 2H_2O$ with DTH using $(\phi\text{-}O)_3P$ as a reducing agent in methanol. The crystals separated out after standing the solution for 12 hours.

Iodo(2,5-dithiahexane)copper(I) Cu(DTH)I

255mg (1.5mmoles) $CuCl_2.2H_2O$ were dissolved in methanol and 183mg (1.5mmoles) DTH added to give a dark green solution. To this solution was added a methanol solution of 455mg (3.0mmoles) $LiI.H_2O$ to produce a cream coloured precipitate. The precipitate was filtered off, washed with dry diethyl ether, and dried under vacuum. The yield was 78% and the crystals went brown at 133° C suggesting decomposition. Analytical results for $CuIC_4H_{10}S_2$: calculated %C=15.22, %H=3.19; observed %C=15.27, %H=3.51.

CHAPTER 4

REACTIVITY STUDIES

4.1 Discussion

These reactivity studies were not meant to be exhaustive but those done are clearly shown.

Both DTH and DTO were readily displaced by a range of monodentate and bidentate ligands. These ligands were: pyridine (py), 2,2'-bipyridyl (bipy), 1,2 diaminoethane (en), trimethylphosinesulphide, sodium dimethyldithiophosphinate dihydrate , and triphenylphosphine.

The reactions:

$Cu(DTH)Cl_2 + \text{xs py} \longrightarrow Cu(py)_2Cl_2$

and $Cu(DTH)Cl + LiCl + \text{xs py} \xrightarrow{\text{air}} Cu(py)_2Cl_2$

have already been studied by Bergen. [22] From these results one would expect that pyridine would also displace the bidentate DTO ligand and this was found to be true for $Cu(DTO)Cl_2$.

Reactions with the bidentate 2,2'-bipyridyl ligand in a 1:1 molar ratio at room temperature, gave similar results with DTH and DTO being easily displaced from $Cu(DTH)Cl_2$ and $Cu(DTO)Cl_2$ to form $Cu(bipy)Cl_2$ and from $Cu(DTH)Cl$ to give $Cu(bipy)Cl$ (which was unstable).

The reactions of ethylenediamine (en) with $Cu(DTO)Cl_2$ and $Cu(DTH)Cl_2$ in a 1:1 molar ratio resulted in the displacement of the respective sulphur ligands to yield $Cu(en)Cl_2$. The reaction of $Cu(DTH)Cl_2$ with ethylenediamine resulted in a green precipitate instead of the characteristic blue, but a dimethylsulfoxide solution was the characteristic blue and the electronic spectrum was identical to that obtained from a dimethylsulfoxide solution of $Cu(en)Cl_2$. The analytical figures provided conclusive evidence that the compound was $Cu(en)Cl_2$.

Trimethylphosphine sulphide, $CH_3P{=}S$, reacted at room temperature with $Cu(DTH)Cl_2$ and $Cu(DTO)Cl_2$ in a Cu: Ligand molar ratio of 1:2, by displacing the respective dithioethers to yield $Cu\,[(CH_3)_3P{=}S]\,Cl$. The same product was obtained on refluxing suspended Cu(DTH)Cl with two moles of trimethylphosphine sulphide in methanol for a few minutes. In all cases the strong $\nu(P{=}S)$ stretching band shifts from $565cm^{-1}$ in the free ligand to $514cm^{-1}$ in the complex. This shift of $50cm^{-1}$ is consistent with bridging phosphinesulfides.[75,76]

Copper(I) reacts with dialkyldithiophosphinates according to the equation $nR_2P(S)S^- + nCu^+ \longrightarrow [R_2P(S)SCu]_n$ $n{=}2$ or 4 whilst Copper(II) reacts according to the equation

$$8R_2P(S)S^- + 4Cu^{2+} \longrightarrow [R_2P(S)SCu]_4 + 2R_2P(S)S_2(S)PR_2$$ [77].

Sodium dimethyldithiophosphinate dihydrate reacted with $Cu(DTH)Cl_2$, $Cu(DTO)Cl_2$, and Cu(DTH)Cl in a 1:1 molar ratio at room temperature to give low yields of $[(CH_3)_2P(S)SCu]_n$. A reaction with $(CuCl)_2DTO$ at room temperature also yielded $[(CH_3)_2P(S)SCu]_n$ but the product contained some starting material (analytical results showed this). The reaction was, therefore, repeated with an excess of the dimethyldithiophosphinate and heated to give a pure product of $[(CH_3)_2P(S)SCu]_n$.

There has been no reported synthesis of $[(CH_3)_2P(S)SCu]_n$ although higher molecular weight dialkyldithiophosphinate analogs have been reported.[77] It was interesting to note that $CuCl_2.2H_2O$ reacted with sodium dimethyldithiophosphinate in a 1:1 molar ratio to give the cream coloured $[CuS(S)P(CH_3)_2]_n$ (n=4?) precipitate. It would, therefore appear that the above equation of Kuchen's for copper(II) and dimethyldithiophosphinate does not hold, as my yield was 85%.

Reactions of triphenylphosphine with $Cu(DTO)Cl_2$ and $Cu(DTH)Cl_2$ at room temperature, in ethanol/methanol solutions, resulted in copper(I) complexes of triphenylphosphine. When $Cu(DTO)Cl_2$ was reacted with an excess of triphenylphosphine the complex $Cu(\phi_3P)_3Cl$ was formed. The reactions of $Cu(DTO)Cl_2$ or $Cu(DTH)Cl_2$ with a two molar equivalent of triphenylphosphine produced the complex $(CuCl)_2(\phi_3P)_3$.

Tayim et al produced $Cu(\phi_3P)_3Cl$ by reacting a concentrated acetone solution of triphenylphosphine with a concentrated acetone solution of the cupric salt using a triphenylphosphine: copper molar ratio of 4:1. Similarly they produced $(CuCl)_2(\phi_3P)_3$ using a 2:1 molar ratio of triphenylphosphine: copper. All other methods of producing these compounds involve refluxing or indirect methods.[78]

Cu(DTH)Cl reacted with triphenylphosphine at room temperature to give the clear crystalline adduct $Cu(DTH)(\phi_3P)Cl$. The infra-red spectrum of this compound showed adsorptions due to both DTH and triphenylphosphine and this was confirmed by analysis. A few mixed ligand complexes involving S and P donor atoms with copper have been reported [79,80,81,82] but in each case one of the sulphur atoms is anionic so this is a new type in which the P and S atoms are only coordinately bonded to the Cu atom.

4.2 Experimental

For a description of the solvents used see chapter 2.4. Pyridine was Hopkin and Williams' General Purpose Reagent stored over KOH and used without further purification; 2,2'-bipyridyl and 1,2-diaminoethane were supplied by B.D.H. Ltd and used without further purification; triphenylphosphine was supplied by Koch-Light Laboratories Ltd. and used without further purification; trimethylphosphinesulphide and sodium dimethyldithiophosphinate dihydrate were supplied by Dr. E.W. Ainscough and used without further purification.

Reactions

$CuCl_2 + xs py \longrightarrow Cu(py)_2Cl_2$ (1)

170mg (1.0mmoles) $CuCl_2.2H_2O$ were dissolved in methanol and a two-fold excess (160mg) pyridine added slowly to give a teal blue precipitate. The precipitate was filtered off, washed with dry diethyl ether, and dried under vacuum. Yield was 99%.

$Cu(DTO)Cl_2 + xspy \longrightarrow Cu(py)_2Cl_2$ (2)

142mg (0.5mmoles) $Cu(DTO)Cl_2$ were dissolved in methanol and a two-fold excess (80mg) pyridine added slowly to give a teal blue precipitate. The blue precipitate was filtered off, washed with dry diethyl ether, and dried under vacuum. The yield was 99%. Compound (2) was identified as $Cu(py)_2Cl_2$ by comparing the infra-red and electronic spectra with those of compound (1).

$Cu(DTO)Cl_2 + bipy \longrightarrow Cu(bipy)Cl_2$ (3)

142mg (0.5mmoles) $Cu(DTO)Cl_2$ were dissolved in methanol and 80mg (0.5mmoles) 2,2'-bipyridyl in a methanol solution was slowly added. A blue-green precipitate formed which was filtered off, washed with dry diethyl ether, and dried under vacuum. The yield was 50%. Compound (3) was identified as $Cu(bipy)Cl_2$ by comparing the infra-red and electronic spectra with those of $Cu(bipy)Cl_2$ prepared by the same method from $CuCl_2.2H_2O$.

$Cu(DTO)Cl_2 + en \longrightarrow Cu(en)Cl_2$ (8)

142mg (0.5mmoles) $Cu(DTO)Cl_2$ were dissolved in methanol and 30mg (0.5mmoles) 1,2diaminoethane added dropwise until a blue precipitate formed. The precipitate was filtered off, washed with dry diethyl ether, and dried under vacuum. The yield was 59%. Compound (8) was identified as $Cu(en)Cl_2$ by comparing the infra-red and visible spectra with those of $Cu(en)Cl_2$ prepared by the same method from $CuCl_2.2H_2O$.

$Cu(DTO)Cl_2 + (CH_3)_2P(S)SNa.2H_2O \longrightarrow [CuS(S)P(CH_3)_2]_n$. (5)

142mg (0.5mmoles) $Cu(DTO)Cl_2$ were dissolved in methanol and 92mg (0.5mmoles) $(CH_3)_2P(S)SNa.2H_2O$ added slowly, as a methanol solution. A cream coloured precipitate formed immediately. The precipitate was filtered off, washed with methanol:water (9:1) solution to remove any precipitated NaCl, washed with dry diethyl ether, and dried under vacuum. The yield was 20%. Analytical results for $C_2H_6PS_2Cu$: calculated %C=12.73, %H=3.21; observed %C=12.88 %H=3.39. $[CuS(S)P(CH_3)_2]_n$ was also prepared from $CuCl_2.2H_2O$ by the same method and the infra-red spectrum compared with that of compound (5) and found to be identical.

$Cu(DTO)Cl_2 + 2(CH_3)_3P{=}S \longrightarrow Cu\,[(CH_3)_3P{=}S]\,Cl$ (9)

142mg (0.5mmoles) $Cu(DTO)Cl_2$ were dissolved in methanol and 108mg (1.0mmoles) $(CH_3)_3P{=}S$ added slowly as a methanol solution. A clear solution resulted, which on standing overnight yielded a white precipitate. The precipitate was filtered off, washed with dry diethyl ether, and dried under vacuum. The yield was 74%. Analytical results for $C_3H_9PSCuCl$: calculated %C=17.40, %H=4.38; observed %C=17.34, %H=4.21. $Cu\,[(CH_3)_3P{=}S]\,Cl$ (8) was also prepared from $CuCl_2.2H_2O$ by the same method and the infra-red spectrum compared with that of compound (9) and found to be identical.

$Cu(DTH)Cl + (CH_3)_3P{=}S \longrightarrow Cu\ (CH_3)_3P{=}S\ Cl$ (19)

110mg (0.5mmoles) of finely ground Cu(DTH)Cl were suspended in methanol and 108mg (1.0mmoles) $(CH_3)_2P{=}S$ added slowly as a methanol solution. The mixture was heated, filtered and allowed to cool. On cooling overnight a white precipitate formed which was filtered off, washed with dry diethyl ether, and dried under vacuum. The yield was 34%. The infra-red spectrum was identical to those of compounds (9) and (14). Analytical results for $C_3H_9ClCuPS$: calculated %C=17.40, %H=4.38; observed %C=17.97, %H=4.53.

$Cu(DTH)Cl + (CH_3)_2P(S)SNa.2H_2O \longrightarrow \left[CuS(S)P(CH_3)_2\right]_n$ (20)

110mg (0.5mmoles) of finely ground Cu(DTH)Cl were suspended in methanol and 92mg (0.5mmoles) $(CH_3)_2P(S)SNa.2H_2O$ added slowly as a methanol solution to give a cream coloured precipitate. The precipitate was filtered off, washed with a methanol:water (9:1) solution to remove any precipitated NaCl, washed with dry diethyl ether, and dried under vacuum. The yield was 50%. Analytical results for $C_2H_6CuPS_2$ calculated %C=12.73, %H=3.21; observed %C=12.72, %H=3.11. The infra-red spectrum of compound (20) was also identical to those of compounds (13) and (5) and also to that prepared from the reaction

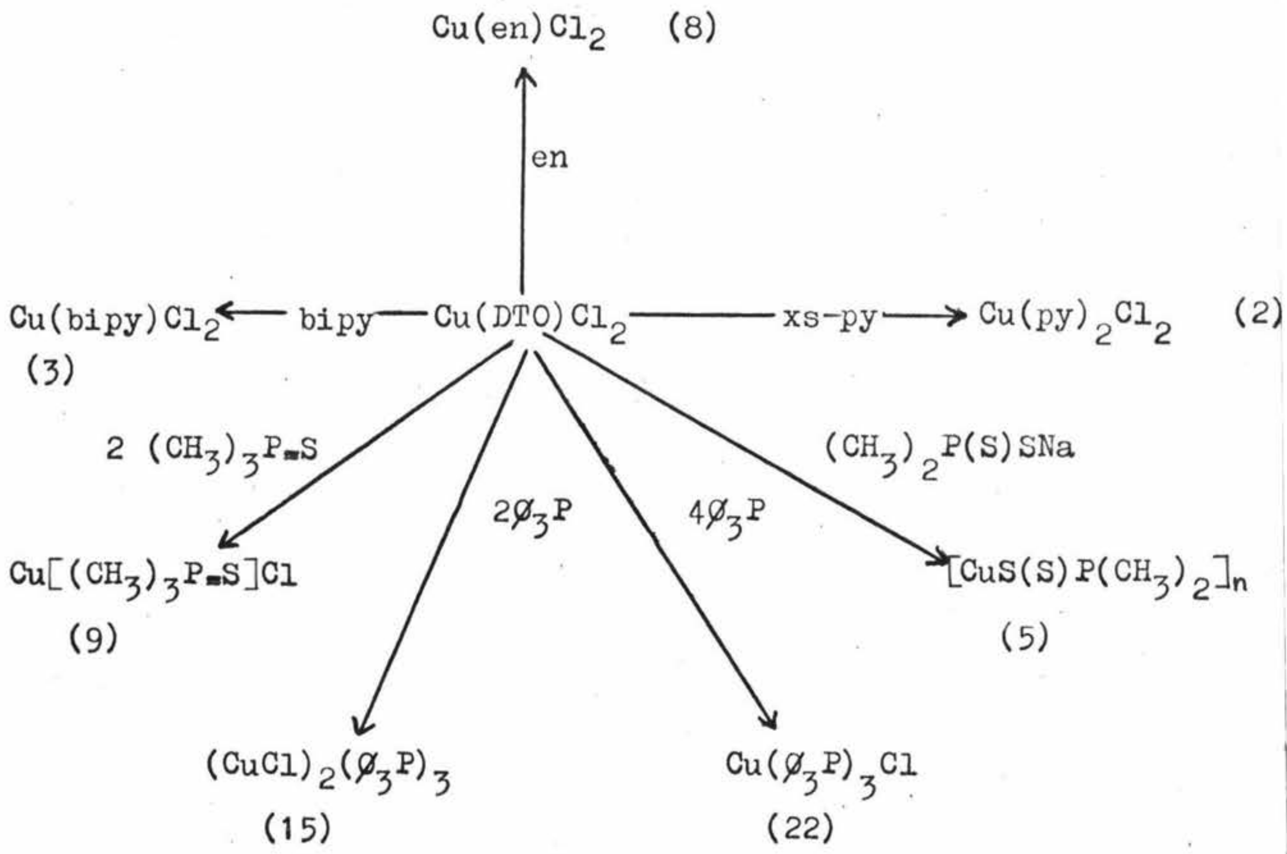
$CuCl_2.2H_2O + (CH_3)_2P(S)SNa.2H_2O \longrightarrow \left[CuS(S)P(CH_3)_2\right]_n$

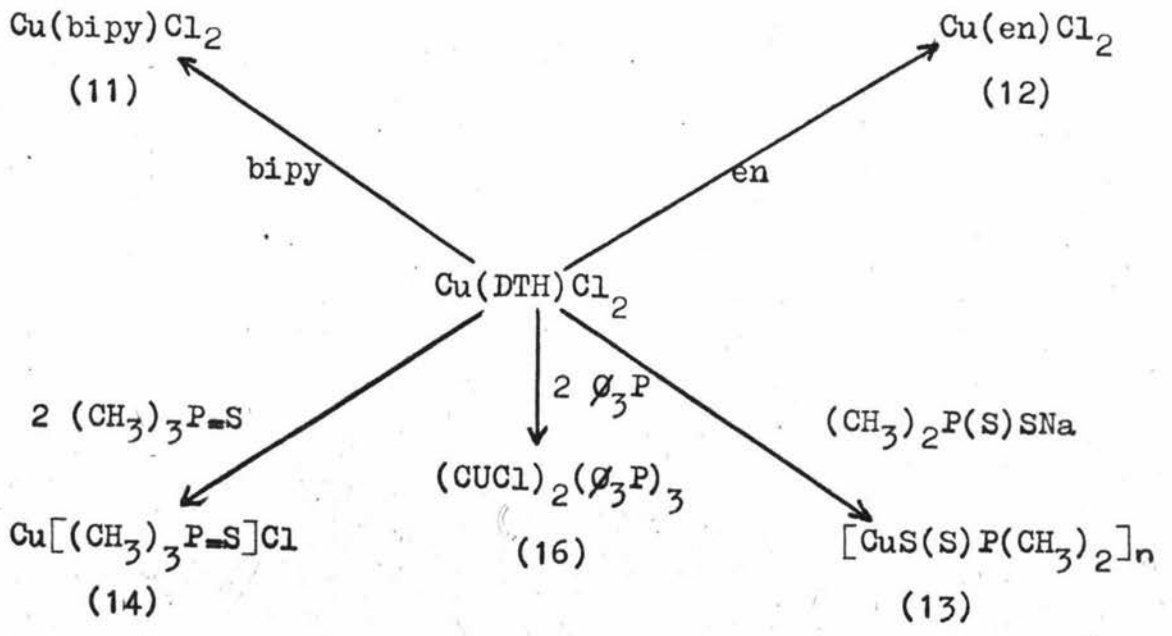
in methanol.

$$Cu(DTH)Cl + \phi_3P \longrightarrow Cu(DTH)(\phi_3P)Cl \qquad (18)$$

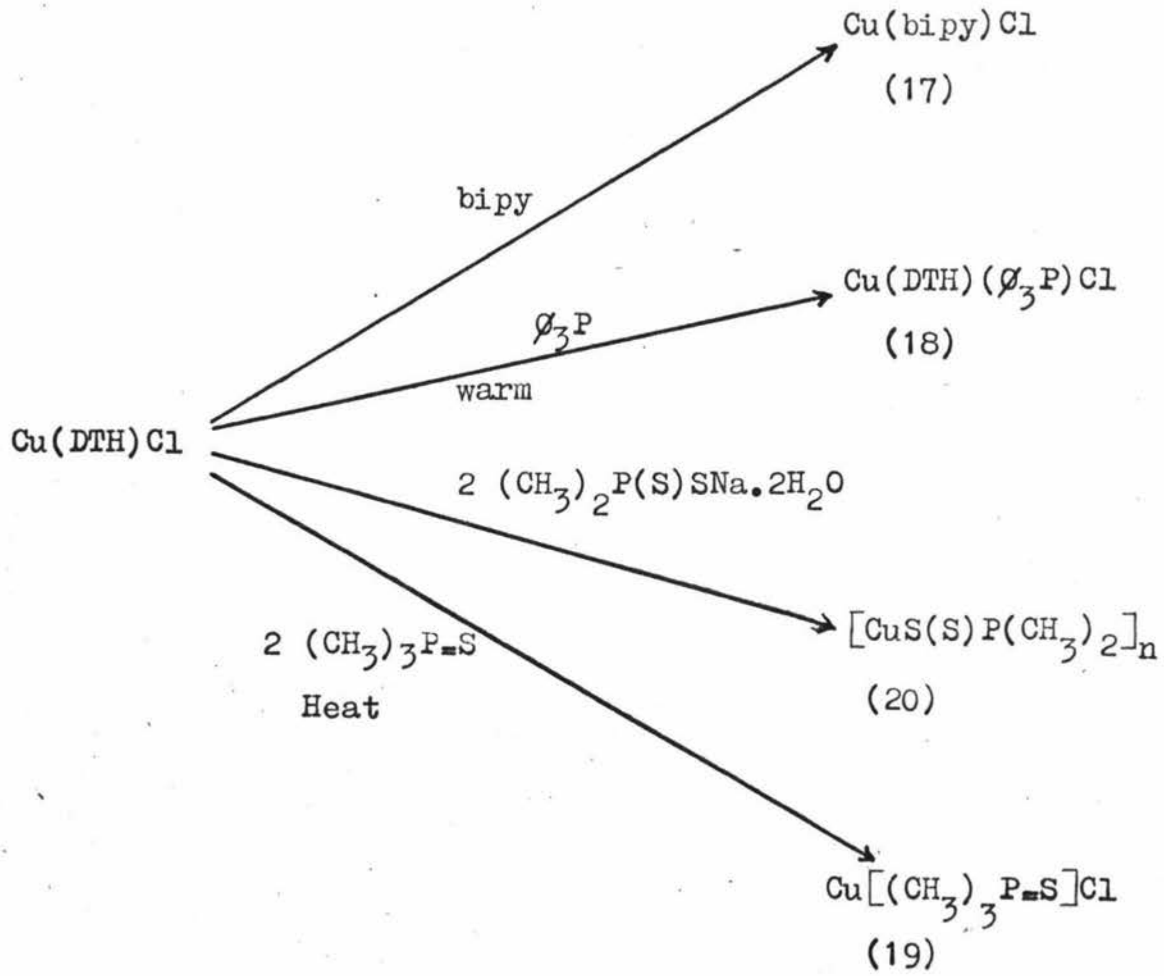
110mg (0.5mmoles) of finely ground Cu(DTH)Cl were suspended in methanol and 131mg (0.5mmoles) triphenylphosphine added as a warm methanol:ethanol (1:1) solution. The mixture was warmed gently until the majority of the suspended material had dissolved, filtered and then allowed to cool. A white crystalline precipitate formed which was filtered off, washed with dry diethyl ether, and dried under vacuum. The yield was 51%. The infra-red spectrum showed the presence of a medium DTH band at 960cm^{-1} and the characteristic triphenylphosphine P-C stretch bands at 508cm^{-1} and 486cm^{-1}. The 3rd P-C stretch was not observed. Analytical results for $C_{22}H_{15}ClCuPS_2$: calculated %C=54.65, %H=5.21; observed %C=54.57, %H=5.31. The proton nuclear magnetic resonance spectrum was recorded in deuterated chloroform. A single peak was observed for each type of proton giving three peaks at; 211ppm for methyl protons, 273ppm for ethyl protons, and 735ppm for the phenyl protons. Tetramethylsilane was used as a reference. The peaks were integrated to give the proton ratio of 15:4:6 for phenyl protons: ethyl protons: methyl protons which corresponds favourably to the theoretical value of 15:4:6. The infra-red showed that the dithiahexane ligand is chelating. The far infra-red spectrum was recorded and a strong band at 246cm^{-1} was assigned as the terminal ν(Cu-Cl) stretching frequency.

REACTION SCHEMES:





REACTION SCHEMES (Continued).



$$(\mathrm{CuCl})_2\mathrm{DTO} \xrightarrow[\text{Heat}]{4\ (\mathrm{CH_3})_2\mathrm{P(S)SNa.2H_2O}} [\mathrm{CuS(S)P(CH_3)_2}]_n$$

(26)

$Cu(DTH)Cl_2 + 2\ \emptyset_3P \longrightarrow (CuCl)_2(\emptyset_3P)_3$ (16)

128mg (0.5mmoles) $Cu(DTH)Cl_2$ were dissolved in methanol and 262mg (1.0mmoles) triphenylphosphine added in a methanol:ethanol (1:1) solution to give a clear solution. On standing overnight clear crystals of $(CuCl)_2(\emptyset_3P)_3$ formed. These crystals were filtered off, washed with dry diethyl ether, and dried under vacuum. The yield was 28%. Analytical results for $C_{54}H_{45}Cl_2Cu_2P_3$: calculated %C=65.85 %H=4.61, %Cl=7.20; observed %C=65.66, %H=4.69, %Cl=7.53. m.p.=232-234° C, Literature m.p.= 232-234° C.

$Cu(DTH)Cl + bipy \xrightarrow{MeOH} Cu(bipy)Cl$ (17)

110mg (0.5mmoles) of finely ground Cu(DTH)Cl were suspended in methanol and 80mg (0.5mmoles) 2,2'-bipyridyl added slowly as a methanol solution to give a red solution of Cu(bipy)Cl. This compound is not easily isolated in a pure form as it oxidises very easily in air to give $Cu(bipy)Cl_2$. However, an electronic spectrum of the red solution was obtained and compared with that of a spectrum of the red solution resulting from the reaction

$CuCl_2.2H_2O + bipy \xrightarrow[N_2]{H_3PO_2} Cu(bipy)Cl_2$

and were found to be identical.

$Cu(DTH)Cl_2 + (CH_3)_2P(S)SNa.2H_2O \longrightarrow CuS(S)P(CH_3)_2$ (13)

128mg (0.5mmoles) $Cu(DTH)Cl_2$ were dissolved in methanol and 92mg (0.5mmoles) $(CH_3)_2P(S)SNa.2H_2O$ slowly added as a methanol solution. A cream coloured precipitate formed immediately. The precipitate was filtered off, washed with a methanol:water (9:1) solution to remove any precipitated NaCl, washed with dry diethyl ether, and dried under vacuum. The yield was 29%. Analytical results for $C_2H_6PS_2Cu$: calculated %C=12.73, %H=3.21; observed %C=13.11, %H=3.24. The infra-red spectrum was also compared with and found to be identical to that of $CuS(S)P(CH_3)_2$ prepared earlier.

$Cu(DTH)Cl_2 + (CH_3)_3P{=}S \longrightarrow Cu\ (CH_3)_3P{=}S\ Cl$ (14)

128mg (0.5mmoles) $Cu(DTH)Cl_2$ were dissolved in methanol and 108mg (1.0mmoles) $(CH_3)_2P{=}S$ added slowly as a methanol solution. A clear solution resulted which on standing overnight gave a white precipitate. The precipitate was filtered off, washed with dry diethyl ether, and dried under vacuum. The yield was 68%. Analytical results for $C_3H_9ClPSCu$: calculated %C=17.40, %H=4.38; observed %C=17.09 %H=4.88.

$Cu(DTH)Cl_2 + bipy \longrightarrow Cu(bipy)Cl_2$ (11)

128mg (0.5mmoles) $Cu(DTH)Cl_2$ were dissolved in methanol and 80mg (0.5mmoles) 2,2'-bipyridyl (bipy) added slowly as a methanol solution. A blue-green precipitate formed which was filtered off, washed with dry diethyl ether and dried under vacuum. The yield was 77%. Compound (11) was identified as $Cu(bipy)Cl_2$ by comparison of infra-red and visible spectra with those of compound 3.

$Cu(DTH)Cl_2 + en \longrightarrow Cu(en)Cl_2$ (12)

128mg (0.5mmoles) $Cu(DTH)Cl_2$ were dissolved in methanol and 30mg (0.5mmoles) 1,2 diaminoethane added dropwise until a green precipitate formed. The precipitate was filtered off, washed with dry diethyl ether, and dried under vacuum. The yield was 50%. Because of the green colour of this compound instead of the blue colour expected a C, H analysis was done to give the following results. Analytical results for $C_2H_8N_3Cl_2Cu$; calculated %C=12.73, %H=3.21; observed %C=12.88, %H=3.39. The infra-red and electronic spectra of compound (12) were compared with those of $Cu(en)Cl_2$ and those of compound (8) and were found to be identical.

$Cu(DTO)Cl_2 + 2\ \phi_3P \longrightarrow (CuCl)_2(\phi_3P)_3$ (15)

142mg (0.5mmoles) $Cu(DTO)Cl_2$ were dissolved in methanol and 262mg (1.0mmoles) triphenylphosphine added slowly in an ethanol:methanol (1:1) solution. A clear solution resulted, which on standing overnight yielded clear crystals of $(CuCl)_2(\phi_3P)_3$. These crystals were filtered off, washed with dry diethyl ether, and dried under vacuum. The yield was 55%. Analytical results for $C_{54}H_{45}P_3Cu_2Cl_2$: calculated %C=65.58, %H=4.61; observed %C=66.07, %H=4.88.m.p.=234-236° C. Literature value for $(CuCl)_2(\phi_3P)_3.C_6H_6$=232-234° C.

$Cu(DTO)Cl_2 + 4\ \phi_3P \longrightarrow Cu(\phi_3P)_3Cl$ (22)

71mg (0.25mmoles) $Cu(DTO)Cl_2$ were dissolved in methanol and 262mg (1.0mmoles) triphenylphosphine added slowly as an ethanol:methanol (1:1) solution. A clear solution resulted which on standing overnight yielded clear crystals of $Cu(\phi_3P)_3Cl$. These crystals were filtered off, washed with dry diethyl ether, and dried under vacuum. The yield was 70%. Analytical results for $C_{54}H_{45}P_3CuCl$: calculated %C=73.22, %H=5.12; observed %C=73.24, %H=5.40. m.p. = 250° C c.f. literature value = 250° C. Crystals went from clear to white at 160° C.

$(CuCl)_2(DTO) + (CH_3)_2P(S)SNa.2H_2O \qquad CuS(S)P(CH_3)_2{}_{n}$ (26)

87mg (0.25mmoles) of finely ground $(CuCl)_2$DTO were suspended in methanol and 92mg (0.5mmoles) $(CH_3)_2P(S)SNa.2H_2O$ added slowly as a methanol solution to give an immediate cream coloured precipitate. The precipitate was filtered off, washed with a methanol:water (9:1) solution to remove any precipitated NaCl, washed with dry diethyl ether, and dried under vacuum. The yield was 86%. Analytical results for $C_2H_6CuPS_2$: calculated %C=12.73, %H=3.21; observed %C=13.37, %H=3.34. The infra-red spectrum of compound (26) was compared with and found to be identical to that of compounds (5), (13), and (20).

CHAPTER 5

INSTRUMENTATION

Infra-red spectra in the range 4000 cm^{-1} to 250 cm^{-1} were recorded as nujol mulls on cesium iodide plates using a Beckmann I.R.20 Spectrophotometer.

Far infra-red spectra in the range 40 cm^{-1} to 290 cm^{-1} were recorded as petroleum jelly mulls on polythene discs using a Grubb-Parsons Cube MkII Interferometer.

Electronic spectra were recorded as nitromethane solutions in the range 25,000 cm^{-1} to 12,500 cm^{-1} using a Beckmann Acta double beam spectrophotometer, and also in the range 25,000 cm^{-1} to 14,000 cm^{-1} using a Perkin-Elmer 124 double beam spectrophotometer with a Perkin-Elmer 165 recorder.

Electronic reflectance spectra were recorded in the range 30,000 cm^{-1} to 5000 cm^{-1} on a Shimadzu MPS 5000 spectrophotometer.

Raman spectra were obtained using an RCA LD 2140 argon ion laser coupled to a Spex 1401 double monochrometer.

X-ray powder photographs were obtained using a Philips PW 1011 X-ray generator coupled to a Philips PW 1352 recording unit.

Conductivities were measured using a Philips PW 9510 conductivity measuring cell with a Philips PR 9500 bridge.

Solvents for spectral work and conductivity measurements were purified as follows;

i) Nitromethane was redistilled over phosphorous pentoxide.

ii) Acetonitrile was purified by method (b) of Walter and Ramaley [83].

Step 1. Reflux impure acetonitrile over anhydrous $AlCl_3$ (15g/l) for 1 hour followed by rapid distillation.

Step 2. Reflux solvent over alkaline permanganate ($KMnO_4$ 10g/l and Li_2CO_3 10g/l) for 15 minutes followed by rapid distillation.

Step 3. Reflux over $KHSO_4$ (15g/l) for 1 hour followed by rapid distillation.

Step 4. Reflux over CaH_2 (2g/l) for 1 hour followed by a careful fractionation from a helice packed column of high reflux ratio, retaining the middle 80%.

iii) Methanol was purified as in chapter 2.4

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