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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

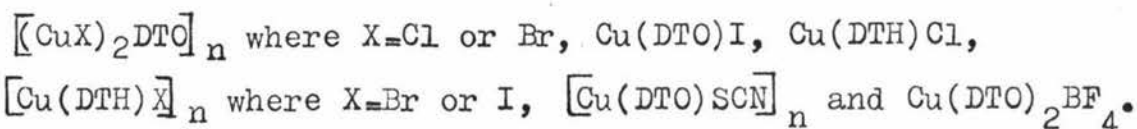
Massey University

October 1975

ABSTRACT

The dithioethers 2,5-dithiahexane (DTH) and 3,6-dithiaoctane (DTO) form the following stable copper (II) complexes; $\text{Cu}(\widehat{\text{S}}\text{S})\text{X}_2$ where $\widehat{\text{S}}\text{S}=\text{DTH}$ or DTO and $\text{X}=\text{Cl}$ or Br , and also $\text{Cu}(\text{DTH})_2(\text{BF}_4)_2$. The complexes $\text{Cu}(\text{DTO})_2(\text{BF}_4)_2$ and $\text{Cu}(\text{DTO})(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ decomposed over a short period of time.

The following copper (I) complexes were also prepared:



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 dimethyldithiophosphate dihydrate, and triphenylphosphine which also forms an adduct with $\text{Cu}(\text{DTH})\text{Cl}$ to give $\text{Cu}(\text{DTH})(\text{C}_6\text{H}_5)_3\text{P}\text{Cl}$.

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CHAPTER 1INTRODUCTION

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)₄¹⁹ whilst it forms bridging complexes with Mo(II)¹¹, Rh(III)^{4,5}, Re(III)^{12,13}, and Cu(I) acetate¹⁵. 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-biotin²². Rheinburger and Sigel²³ commented that the interactions between simple thioethers and biologically important metal-ions like Mn²⁺, Cu²⁺, Zn²⁺ 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)Cl₂^{8,14,22}, Cu(DTH)Cl¹⁴, Cu(DTH)Br¹⁴, Cu(DTO)Cl₂¹⁷, Cu(DTH)₂(BF₄)₂^{8,22}, Cu(DTH)₂(ClO₄)₂^{8,22} and (CuOOCCH₃)₂DTH¹⁵.

A recent development is the discovery of Cu(II) and Fe(III) complexes of N-methylthioformylhydroxamic acid in the culture broth of Pseudomonas fluorescens²⁴. 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' culture²⁴. 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 al²⁵ 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 270cm⁻¹ to be a (Cu-S) stretching frequency.

Further evidence of copper sulphur bonding in proteins is from x-ray photoelectron spectroscopy²⁶ 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)! 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 2COPPER(II) COMPLEXES2.1 Syntheses

The following copper(II) complexes were prepared:

Cu(DTH)X_2 where $\text{X}=\text{Cl}$ or Br ; Cu(DTO)X_2 where $\text{X}=\text{Cl}$ or Br ;
 $\text{Cu(DTO)}_2(\text{BF}_4)_2$; and $\text{Cu(DTO)(NO}_3)_2 \cdot \text{H}_2\text{O}$.

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 Weissburger⁷ 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 $\text{CuBr}_2(\text{anhydrous})$.

The nitrate 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) tetrafluoroborate 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 nitrate 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 $\text{Cu(DTH)}_2\text{X}_2$ where $\text{X}=\text{BF}_4$ or ClO_4 ^{8,22} and $\text{Cu(DTH)}_2\text{BF}_4$ ²². The tetrafluoroborate 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 1600cm^{-1} to 600cm^{-1} for the complexes $\text{Cu}(\text{DTH})\text{X}_2$ where $\text{X}=\text{Cl}$ or Br show the same pattern of ligand bands as $\text{Cu}(\text{DTH})_2(\text{BF}_4)_2$, 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 $\text{Cu}(\text{DTO})_2(\text{BF}_4)$ 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 tetragonally distorted environment around the copper atom in $\text{Cu}(\text{DTH})_2(\text{BF}_4)_2$ 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 1050cm^{-1} and 970cm^{-1} that are very broad, and also a band at 510cm^{-1} . A sharp medium intensity band also occurs at 760cm^{-1} . Nakamoto²⁸ reports the spectra of ionic BF_4 as $\nu_1=769\text{cm}^{-1}$; $\nu_2=353\text{cm}^{-1}$; $\nu_3=984\text{cm}^{-1}$; and $\nu_4=524\text{cm}^{-1}$. 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 $\text{Cu}(\text{DTH})_2(\text{BF}_4)_2$ 27

Where DTH=2,5-dithiahexane.

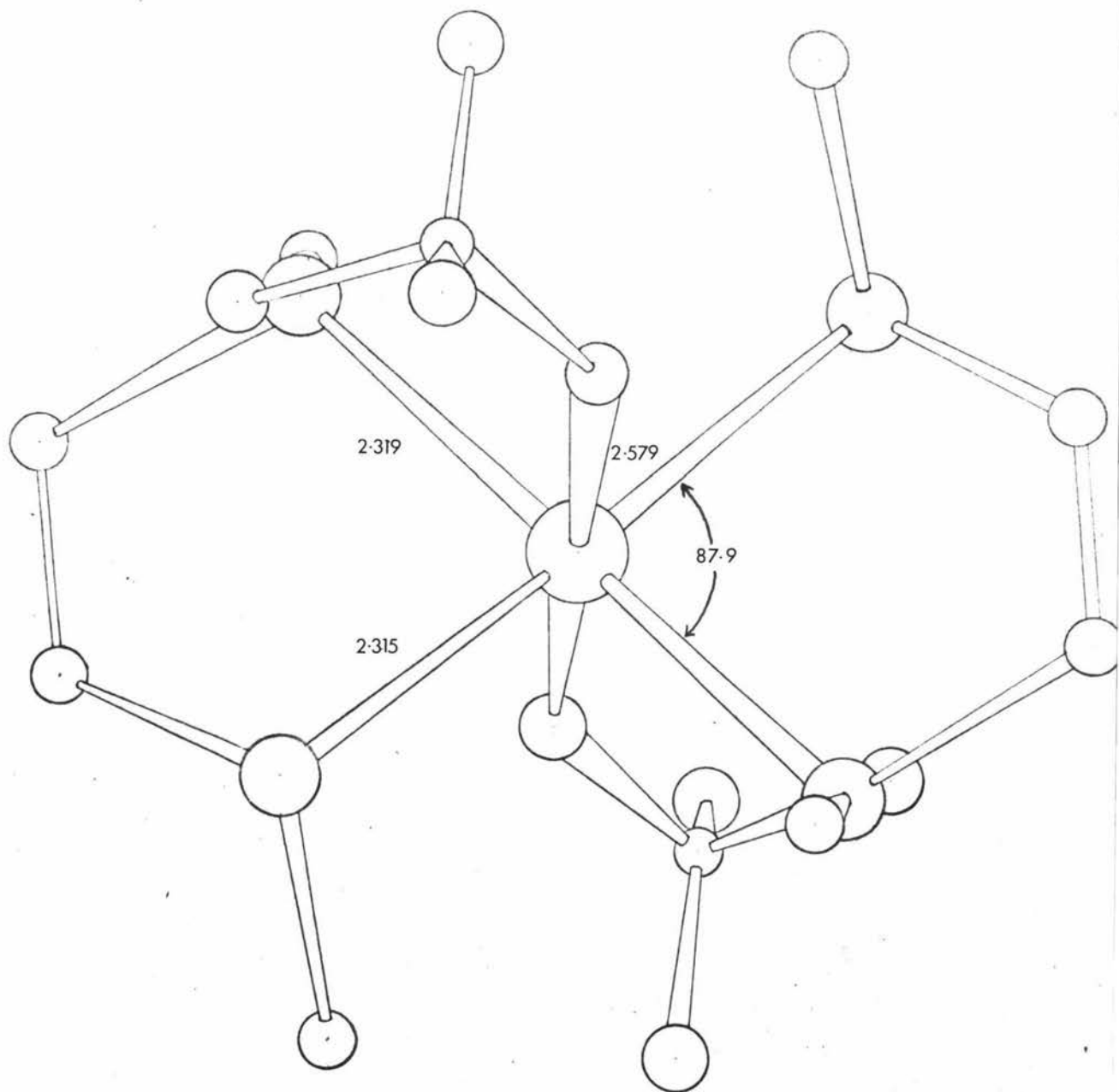
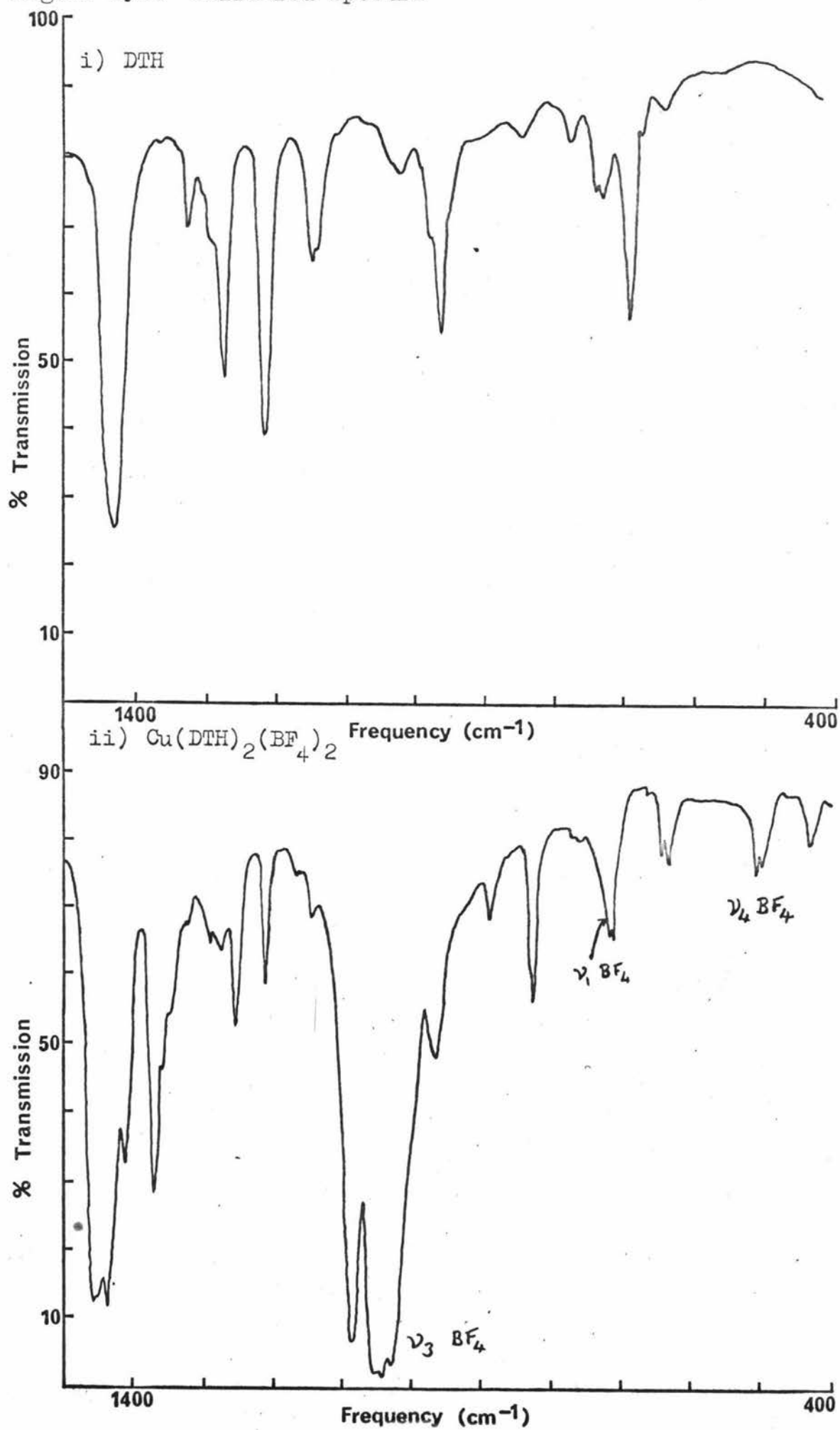
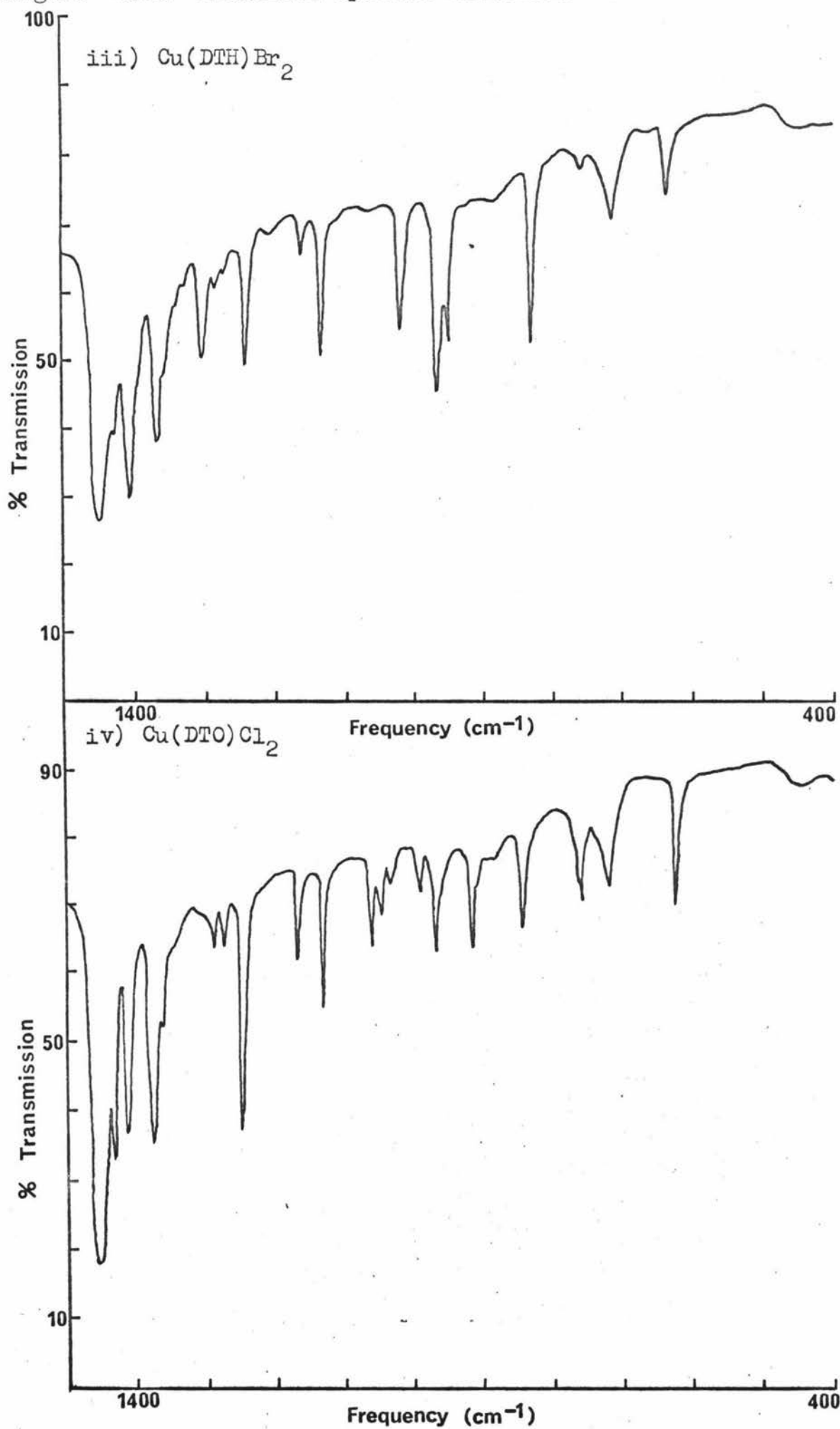


Figure 2.2b Infra-red Spectra





an extra weak band at 768cm^{-1} in $\text{Cu}(\text{dien})(\text{BF}_4)_2 \cdot \text{H}_2\text{O}$ 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 $\text{Cu}(\text{en})_2(\text{BF}_4)_2$, which has weakly coordinated BF_4 groups with Cu-F distances of 2.56\AA . The infra-red spectral data is therefore, consistent with structure. This same pattern occurred in the infra-red spectrum of $\text{Cu}(\text{DTO})_2(\text{BF}_4)_2$ 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 $\text{Cu}(\text{DTO})_2(\text{BF}_4)_2$ and $\text{Cu}(\text{DTH})_2(\text{BF}_4)_2$ may be isostructural.

The x-ray powder photographs show similar patterns of 2θ and d for $\text{Cu}(\text{DTO})\text{Cl}_2$ and $\text{Cu}(\text{DTO})\text{Br}_2$ indicating that these two compounds have very similar structures in the solid state. $\text{Cu}(\text{DTH})\text{Cl}_2$ and $\text{Cu}(\text{DTH})\text{Br}_2$ 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 $\text{Cu}(\text{DTH})_2(\text{BF}_4)_2$ it would appear that the $\nu(\text{Cu-S})$ 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

<u>Cu(DTO)Cl₂</u>				<u>Cu(DTO)Br₂</u>			
	<u>2θ</u>	<u>d</u>	<u>Relative Intensity</u>		<u>2θ</u>	<u>d</u>	<u>Relative Intensity</u>
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 Å,
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

X-ray generator Philips PW 1011 using Philips Pw 1352 recording unit.

Table 2.3c continued.

<u>Cu(DTH)Cl₂</u>				<u>Cu(DTH)Br₂</u>			
	<u>2θ</u>	<u>d</u>	<u>Relative Intensity</u>		<u>2θ</u>	<u>d</u>	<u>Relative Intensity</u>
1.	14.30	7.18	s	1.	13.29	7.73	w
2.	16.65	6.18	vs	2.	13.81	7.44	vs
3.	17.35	5.93	w-m	3.	16.29	6.31	vs
4.	19.27	5.34	w	4.	18.62	5.53	w-m
5.	22.02	4.68	w	5.	19.89	5.18	w-m
6.	22.60	4.56	w	6.	22.80	4.52	m-s
7.	25.40	4.07	m	7.	23.15	4.46	vs
8.	26.20	3.95	vw	8.	23.77	4.34	vw
9.	26.64	3.88	vw	9.	25.55	4.05	vw
10.	27.57	3.75	w-m	10.	26.73	3.87	w-m
11.	29.15	3.55	s	11.	27.23	3.80	m-s
12.	30.21	3.43	vw	12.	27.75	3.73	m
13.	31.31	3.31	w	13.	28.09	3.69	m
14.	32.10	3.23	s	14.	29.60	3.50	w
15.	32.35	3.21	vs	15.	30.06	3.45	m
16.	32.66	3.18	s	16.	30.67	3.38	m
17.	34.25	3.04	m	17.	32.80	3.17	vs
18.	36.72	2.84	vw	18.	33.64	3.09	w-m
19.	38.40	2.72	m-s	19.	34.45	3.02	m-s
20.	40.80	2.57	s	20.	36.10	2.89	vw
21.	41.31	2.54	w-m	21.	36.72	2.84	vw
22.	43.00	2.44	vw	22.	37.25	2.80	vw
23.	45.10	2.33	w	23.	38.12	2.74	m-s
24.	45.37	2.32	w-m	24.	39.15	2.67	w
25.	47.20	2.23	w	25.	39.85	2.62	vw
26.	47.65	2.21	w	26.	40.20	2.60	vw
27.	49.95	2.12	vs	27.	40.86	2.56	vs
28.	51.42	2.06	w	28.	42.00	2.50	w
29.	53.25	1.99	w-m	29.	42.58	2.46	vw
30.	54.55	1.95	vw	30.	43.23	2.43	w
31.	55.47	1.92	w	31.	44.72	2.35	w-m
32.	57.90	1.85	vw	32.	46.48	2.27	vw
33.	58.18	1.84	w	33.	46.60	2.26	vw
34.	60.30	1.78	w	34.	47.24	2.23	w
35.	61.60	1.75	w	35.	49.93	2.12	m-s
36.	63.70	1.70	m	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 Å
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

<u>Compound</u>	<u>Instrument</u>	<u>Absorption Maxima (cm⁻¹)</u>		
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 $\approx 259\text{cm}^{-1}$ 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 $\text{Cu}(\text{DTH})\text{Cl}_2$ Flint and Goodgame⁸ assigned a strong band at 308cm^{-1} as $\nu(\text{Cu-Cl})$ 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 $\text{Cu}(\text{DTH})_2(\text{ClO}_4)_2$; and strong bands at 291cm^{-1} , 274cm^{-1} and 255cm^{-1} for $\text{Cu}(\text{DTH})_2(\text{BF}_4)_2$ but did not assign these. Petillon et al³² assigned bands in the region 272cm^{-1} to 310cm^{-1} as $\nu(\text{Cu-S})$ stretch for the complexes CuL_2X where $\text{L}=\text{C}_3\text{H}_2\text{S}_3$ and $\text{X}=\text{Cl}$ or Br . As a result of these considerations the $\nu(\text{Cu-S})$ stretching frequencies appear to be in the range 296cm^{-1} to 280cm^{-1} .

Lever and Ramaswamy³³ assigned bands in the range 294cm^{-1} to 305cm^{-1} to $\nu(\text{Cu-Cl})$ 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 $\text{Cu}(2\text{-methylpyridine})_2\text{X}_2$ (where $\text{X}=\text{Cl}$ or Br) and the sixth coordination site being blocked by the 2-methyl group.


Lever and Mantovani³⁴ assigned strong bands above 300cm^{-1} for copper(II) chloride complexes of $\text{N,N}'$ -dialkylethylenediamines, $\text{Cu}(\text{sym-R}_2\text{-en})\text{Cl}_2$ where $\text{R}=\text{methyl}$ or ethyl groups, to be those of $\nu(\text{Cu-Cl})$ stretching frequencies. Considering $\text{Cu}(\text{DTO})\text{Cl}_2$ and $\text{Cu}(\text{DTH})\text{Cl}_2$ it would appear that the $\nu(\text{Cu-Cl})$ stretching frequencies may be tentatively assigned to 312cm^{-1} and 302cm^{-1} for $\text{Cu}(\text{DTO})\text{Cl}_2$ and 308cm^{-1} for $\text{Cu}(\text{DTH})\text{Cl}_2$. These assignments are also based on the fact that these are not

observed in the analogous bromide complexes or the $\text{Cu(L)}_2(\text{BF}_4)_2$ complexes, where $\text{L}=\text{DTO}$ or DTH . Lever and Ramaswamy³³ assigned bands in the region 218cm^{-1} to 255cm^{-1} as $\nu(\text{Cu-Br})$ stretching frequencies for the bromo analogs of the above substituted pyridine complexes. Lever and Mantovani³⁴ assigned medium bands at 227cm^{-1} to 229cm^{-1} for the bromo analogs of their substituted ethylenediamine complexes as $\nu(\text{Cu-Br})$ stretching frequencies. The strong bands at 256cm^{-1} (251cm^{-1} sh) and 243cm^{-1} in $\text{Cu}(\text{DTO})\text{Br}_2$ and the strong bands at 257cm^{-1} and 253cm^{-1} in $\text{Cu}(\text{DTH})\text{Br}_2$ may be assigned to $\nu(\text{Cu-Br})$ stretching frequencies. These are assigned because of their intensity, their position in relation to those assigned by Lever and Mantovani³⁴ and Lever and Ramaswamy³³ and their position in relation to the copper-chlorine stretches where the ratio $\nu(\text{Cu-Br})/\nu(\text{Cu-Cl}) \simeq 0.8$

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 $\text{Cu}(\text{DTO})\text{Br}_2$ and $\text{Cu}(\text{DTH})\text{Br}_2$ were not sufficiently soluble in nitromethane for molecular weight measurements, but were measured in methanol. The complexes $\text{Cu}(\text{DTO})\text{Cl}_2$ and $\text{Cu}(\text{DTH})\text{Cl}_2$ 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.

<u>Compound</u>	<u>Solvent</u>	<u>M.W. Obs.</u>	<u>M.W. Calc.</u>	
Cu(DTO)Cl ₂	CH ₃ OH	286	284.75	61.50
	CH ₃ NO ₂	266	284.75	10.92
Cu(DTH)Cl ₂	CH ₃ OH	171	256.70	—
	CH ₃ NO ₂	279	256.70	4.56
Cu(DTO)Br ₂	CH ₃ OH	368	373.66	—
	CH ₃ NO ₂	—	373.66	18.93
Cu(DTH)Br ₂	CH ₃ OH	272	345.61	—
	CH ₃ NO ₂	—	345.61	20.42
Cu(DTH) ₂ (BF ₄) ₂	CH ₃ NO ₂	—	481.66	197.03

$$x = \text{mhos cm}^2$$

From the molecular weight data in Table 2.3a it appears that Cu(DTO)Cl₂ and Cu(DTO)Br₂ are monomeric in methanol, whilst the values for Cu(DTH)Cl₂ and Cu(DTH)Br₂ are unusually low. The low value for Cu(DTH)Cl₂ may be due to some dissociation of the chloro group and that of Cu(DTH)Br₂ may be due to its ease of reduction in solution (especially on heating). Both Cu(DTO)Cl₂ and Cu(DTH)Cl₂ 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)Cl₂ is also a non-electrolyte in methanol. Cu(DTH)₂(BF₄)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 $\text{Cu}(\text{DTH})_2(\text{BF}_4)_2$ which was diluted with MgO .

In all complexes a ligand charge-transfer band was recorded in the range $42,700\text{cm}^{-1}$ to $45,500\text{cm}^{-1}$. The free DTH ligand has a band at $43,100\text{cm}^{-1}$ and DTO a band at $41,800\text{cm}^{-1}$, 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 Hathaway³⁵ 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 Mantovani³⁴ in their investigations of ethylenediamine complexes assign a shoulder at $\approx 14,000\text{cm}^{-1}$ to the $z^2 \rightarrow x^2 - y^2$ 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 ($xy \rightarrow x^2 - y^2$, $xz \rightarrow x^2 - y^2$, $yz \rightarrow x^2 - y^2$). Lever and Mantovani³⁶ 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

<u>Compound</u>	<u>Other Bands (cm⁻¹)</u>		<u>d-d Transitions (cm⁻¹)</u>		<u>State of Compound</u>
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;35,700 ^{vw} ,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 coordinating) 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.

$\text{Cu}(\text{DTH})_2(\text{BF}_4)_2$ has a d-d band at $18,700\text{cm}^{-1}$ in the solid state. This is comparable to $19,510\text{cm}^{-1}$ for $\text{Cu}(\text{en})_2(\text{BF}_4)_2$, $18,790\text{cm}^{-1}$ for $\text{Cu}(\text{sym-Me}_2\text{-en})_2(\text{BF}_4)_2$, and $18,650\text{cm}^{-1}$ for $\text{Cu}(\text{sym-Et}_2\text{-en})_2(\text{BF}_4)_2$ in the solid state reported by Lever and Mantovani³⁶. The crystal structures of both $\text{Cu}(\text{DTH})_2(\text{BF}_4)_2$ and $\text{Cu}(\text{en})_2(\text{BF}_4)_2$ 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. $\text{CuX}_2(\text{CH}_3\text{CN})_n$ where $n = \frac{1}{2}, 1$, or 2 .³⁷

The solid reflectance spectra of $\text{Cu}(\text{DTO})\text{Cl}_2$, $\text{Cu}(\text{DTH})\text{Cl}_2$, and $\text{Cu}(\text{DTO})\text{Br}_2$ show d-d bands in the region $12,350\text{cm}^{-1}$ to $12,800\text{cm}^{-1}$ indicating that there is much less tetragonal

distortion in these complexes than in $\text{Cu}(\text{DTH})_2(\text{BF}_4)_2$ and, therefore, 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 $23,400\text{cm}^{-1}$ to $25,000\text{cm}^{-1}$ for substituted thiourea complexes of copper(II) perchlorates ³⁸, $22,900\text{cm}^{-1}$ to $23,800\text{cm}^{-1}$ for copper(II)-bis(diethyldithiocarbamate) ^{39, 40} and $23,000\text{cm}^{-1}$ for copper(II)-bis(di-isopropyldithiocarbamate) ³⁹. On this basis the bands in the region $22,700\text{cm}^{-1}$ to $25,100\text{cm}^{-1}$ 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 $\text{Cu}(\text{N-N})_2\text{Cl}_2$ ⁴¹ (where N-N is ethylenediamine, sym-dimethylethylenediamine, or sym-diethylethylenediamine) in the range $36,800\text{cm}^{-1}$ to $33,500\text{cm}^{-1}$. The following chlorine to copper charge transfer bands have also been reported ⁴¹ $18,000\text{cm}^{-1}$ for CuCl_2 , $22,000\text{cm}^{-1}$ to $25,000\text{cm}^{-1}$ for CuCl_4^{2-} , and $24,200\text{cm}^{-1}$ for CuCl_5^{3-} . On this basis the solid reflectance bands at $27,800\text{cm}^{-1}$ for $\text{Cu}(\text{DTO})\text{Cl}_2$ and $27,400\text{cm}^{-1}$ for $\text{Cu}(\text{DTH})\text{Cl}_2$ may be assigned to chlorine to copper charge transfer bands. The bands at $35,700\text{cm}^{-1}$ to $38,900\text{cm}^{-1}$ do not appear to be halide to copper charge transfer bands as a band at $35,700\text{cm}^{-1}$ is present in $\text{Cu}(\text{DTH})_2(\text{BF}_4)_2$. 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)Br₂ and Cu(DTH)Br₂ can not be assigned with confidence, however, in acetonitrile solutions bands at 28,200cm⁻¹ 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.

$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, CuO , $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, 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

$\text{Cu}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ 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.

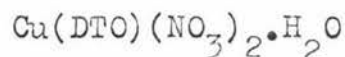
Dibromo(3,6-dithiaoctane)copper(II)

This compound could not be isolated from solution and was therefore, prepared by a method used by Carlin and Weissburger⁷ in their syntheses of cobalt(II) complexes of DTO.

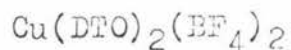
223mg (1.0mmoles) of finely ground CuBr_2 was placed in a 5ml beaker and excess DTO (5.0mmoles=0.5mls) added to cover the CuBr_2 . This mixture was left to react for 15 minutes. The dark brown product was filtered to remove the excess DTO, washed with dry diethyl ether and dried under vacuum. The yield was 95% and the m.p. = 129-131° C. Analytical results for $\text{CuBr}_2\text{C}_6\text{H}_{14}\text{S}_2$: 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)

852mg (5.0mmoles) $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ 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 $\text{C}_6\text{H}_{14}\text{S}_2\text{CuCl}_2$: 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

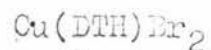
242mg (1.0mmoles) $\text{Cu(NO}_3)_2 \cdot 3\text{H}_2\text{O}$ were dissolved in DMP and 150mg (1.0mmoles) DTO were added dropwise to give a dark green precipitate. This was filtered off, washed with dry diethyl ether, and dried under vacuum. An oil resulted when the compound was prepared in either acetone or ethanol. The yield was 56% and the m.p. was not obtained. Analytical results for $\text{CuN}_2\text{O}_7\text{C}_6\text{H}_{16}\text{S}_2$: 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

173mg (0.5mmoles) $\text{Cu}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ were dissolved in TLOF 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 $\text{CuB}_2\text{F}_8\text{C}_{12}\text{H}_{28}\text{S}_4$: 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)

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)

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 $\text{CuBr}_2\text{C}_4\text{H}_{10}\text{S}_2$: 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-O₂)

On standing, the complex $\text{Cu}(\text{DTO})(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ 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 $\text{Cu}(\text{DTO})(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$, but with much stronger and broader water bands, and two extra bands in the region 1200cm^{-1} to 1300cm^{-1} . These bands were thought to be $\nu(\text{S}=\text{O})$ 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; $\text{Cu}(\text{DTO-O}_2)\text{Cl}_2$, $\text{Cu}(\text{DTO-O}_2)(\text{NO}_3)_2$, $\text{Cu}(\text{DTO-O}_2)_2(\text{BF}_4)_2$ and $\text{Cu}(\text{DTO-O}_2)_2(\text{PF}_6)_2$. 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, $\text{Cu}(\text{DTO-O}_2)\text{Cl}_2$, $\text{Cu}(\text{DTO-O}_2)(\text{NO}_3)_2$ and $\text{Cu}(\text{DTO-O}_2)_2(\text{PF}_6)_2$ gave good analyses, whilst that of $\text{Cu}(\text{DTO-O}_2)_2(\text{BF}_4)_2$ 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-O₂) 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 Bennett⁴² two isomers of 2,5-dithiahexane-2,5-dioxide (DTH-O₂) 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 $\nu(\text{S=O})$ stretching frequencies at 1019cm^{-1} and 1047cm^{-1} in the free ligand to between 900cm^{-1} and 950cm^{-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 1100cm^{-1} and 1150cm^{-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 $\text{Cu}(\text{DTO})(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ compound was compared with those of the above prepared complexes no conclusions could be made about the two extra bands in the 1200cm^{-1} to 1250cm^{-1} region for the light green $\text{Cu}(\text{DTO})(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ 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.

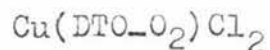
3,6-dithiaoctane-3,6-dioxideDTO-O₂

11.4g (0.76moles) 3,6-dithiaoctane were added slowly to a stirred solution of 100ml glacial acetic acid (CH₃COOH) with 20g of 30% hydrogen peroxide (H₂O₂). 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.

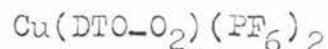
Dinitrato(3,6-dithiaoctane-3,6-dioxide)copper(II)Cu(DTO-O₂)(NO₃)₂

241mg (1.0mmoles) Cu(NO₃)₂·3H₂O was dissolved in triethylorthoformate (TEOF). 182mg (1.0mmoles) DTO-O₂ 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 infra-red 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 C₆H₁₄S₂O₈N₂Cu: 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)

170mg (1.0mmoles) $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ were dissolved in ethanol and 5mls of 2,2-dimethoxypropane (DMP) added. 182mg (1.0mmoles) DTO-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 $\text{C}_6\text{H}_{14}\text{S}_2\text{O}_2\text{Cl}_2\text{Cu}$: 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

174mg (0.5mmoles) $\text{Cu}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ were dissolved in acetone and an equal amount of DMP added. A second solution containing 182mg (1.0mmoles) DTO-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 $\text{C}_6\text{H}_{14}\text{S}_2\text{O}_2\text{P}_2\text{F}_{12}\text{Cu}$: calculated %C=22.45, %H=4.40; observed %C=22.03, %H=4.09.

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



348mg (1.0mmoles) $\text{Cu}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ were dissolved in DMP and heated until the solution changed colour from blue to green. To this solution was added 364mg (2.0mmoles) DTO-O₂ 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-O₂. The m.p. was not determined because of the presence of ligand. Analytical results for $\text{C}_6\text{H}_{14}\text{S}_2\text{O}_2\text{B}_2\text{F}_8\text{Cu}$: calculated %C:23.95, %H=4.69; observed %C=24.32, %H=5.74.