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TRANSITION METAL COMPLEXES OF THIOSEMICARBAZIDE AND THIOSEMICARBAZONES

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CONTENTS

ABBREVIATIONS

TSC	thiosemicarbazide
TSDA	thiosemicarbazide diacetic acid
SDA	semicarbazide diacetic acid
4EtTSC	4-ethyl thiosemicarbazide
2PATSC	2-pyridinaldehyde thiosemicarbazone
ISTSC	isatin thiosemicarbazone
MeISTSC	1-methyl isatin thiosemicarbazone
PVATSC	pyruvic acid thiosemicarbazone
SALTSC	salicylaldehyde thiosemicarbazone
MePVTSC	methyl pyruvate thiosemicarbazone
8QATSC	8-quinolinaldehyde thiosemicarbazone
TSCAC	acetone thiosemicarbazone
CHTSC	cyclohexanone thiosemicarbazone
H_2KTS	3-ethoxy-2-oxobutanone bis(thiosemicarbazone)

DMSO	dimethylsulphoxide
DMF	dimethylformaldehyde
DAOTSC	diacetyl monoxime thiosemicarbazone
DAOMeTSC	*O*-methyl diacetyl monoxime thiosemicarbazone
TSC-2,5-D	hexane-2,5-dione bis(4-methyl thiosemicarbazone)
TSCPHAL	phthalaldehyde bis(4-methyl thiosemicarbazone)
1-FIQTSC	1-formylisoquinoline thiosemicarbazone
2-FPYTSC	2-formylpyridine thiosemicarbazone
BUTSC	butyraldehyde

A. INTRODUCTION

Thiosemicarbazide ($NH_2CSNHNH_2$) and thiosemicarbazones ($NH_2CSNHN{=}CR_1R_2$) usually react as chelating ligands with transition metal ions by bonding through the sulphur and hydrazinic nitrogen atoms, although in a few cases they behave as monodentate ligands and bond through the sulphur atom only.

In view of the potential interest in ligands with SN donor atom sets it is curious that relatively few transition metal complexes of thiosemicarbazide have been prepared and studied in any detail. Among those which have been studied a surprising number are compounds of nickel(II) and were originally prepared by Jensen [1] in his pioneering work over 35 years ago!

Since Domagk's original report [2] on the anti-tubercular activity of thiosemicarbazones the number of papers on the pharmacology of these compounds has expanded dramatically. They have also been found to be active against influenza [3], protozoa [4], smallpox [5], and certain kinds of tumour [6], and have been suggested as possible pesticides [7] and fungicides [8]. Their activity has frequently been thought to be due to their ability to chelate trace metals. Thus Liebermeister [9] showed that copper ions enhance the anti-tubercular activity of *p*-acetamidobenzaldehyde thiosemicarbazone. Similarly Petering and co-workers [10] showed that the active intermediate in the anti-tumour activity of 3-ethoxy-2-oxobutyraldehyde bis(thiosemicarbazone) (H_2KTS) was the chelate Cu(KTS). These findings have led recently to an increased interest in the chemistry of transition metal chelates of thiosemicarbazones.

B. THERMODYNAMIC DATA

There is very little thermodynamic data available for the transition metal complexes of TSC and virtually none for those of thiosemicarbazones. The successive formation constants for complexes formed by TSC with some transition metal ions are shown in Table 1. The values in parentheses are the corresponding values for the complexes of semicarbazide ($NH_2CONHNH_2$), the oxygen analogue of TSC, which are included for the purpose of comparison. The complex equilibria involved are represented, except in the case of Hg(II), by the equation

TABLE 1

(a) Stability constants of complexes with thiosemicarbazide

	Ni(II)	Cu(II)	Zn(II)	Cd(II)	Hg(II)	Ru(III)	H(I)
log β_1	ca. 2.7	6.0 ^{a} 6.11 ^{b} (3.2) ^{a}	(2.3) ^{c}	2.5 ^{c} 2.6 ^{d} (1.5) ^{c}		^{e}	1.50 ^{e} 2.0 ^{g}
log β_2		11.6 ^{a} 11.48 ^{b} (6.60) ^{a}	ca. 2.8 ^{c} (3.7) ^{c}	4.3 ^{c} 4.7 ^{f} 5.5 ^{g} (3.0) ^{c}	22.4 ^{c} (11.6) ^{c}		
log β_3				ca. 6.0 ^{c} 5.9 ^{f}	24.8 ^{c} (15.2) ^{c}		
log β_4					25.8 ^{h}		

[a] Ref. 15. [b] Ref. 14. [c] Ref. 11. [d] Ref. 17. [e] Ref. 18. [f] Ref. 17. [g] Ref. 16. [h] Ref. 19.
Values in parentheses refer to semicarbazide complexes.

(b) Stability constants of complexes with thiosemicarbazide *N,N*-diacetic acid [12]

	Mn(II)	Co(II)	Ni(II)	Cu(II)	Zn(II)	Cd(II)
log β_1	2.0 (2.6)	5.4 (5.9)	5.9 (6.4)	8.1 (8.4)	5.8 (6.6)	7.4 (5.7)

Values in parentheses refer to complexes with semicarbazide *N,N*-diacetic acid [12].

$$M(H_2O)_6^{2+} + n\text{TSC} \rightleftharpoons [M(H_2O)_{6-2n}\text{TSC}_n]^{2+} + 2nH_2O$$

In the case of Hg(II) the very similar values of log β_3 found for the TSC and thiourea complexes lead us to the conclusion that TSC is behaving as a monodentate ligand. Comparison of these values with the corresponding values for the oxygen and selenium analogues of both TSC and thiourea leaves little doubt that coordination is through sulphur [11]. The data for thiosemicarbazide *N,N*-diacetic acid (TSDA), and for its oxygen analogue (SDA) have also been included in Table 1. This has been done firstly because the ionisation constants of the ligand acids are virtually identical [12] and any difference between their stability constants with a given metal ion will mainly reflect differences in bonding with sulphur and oxygen (both ligands are tetradentate with the donor atom set O_2NX where X = O or S). The enthalpy changes have been determined directly by calorimetry [12], providing a second and more important reason for including these data.

Table 2 contains free energy, enthalpy and entropy changes accompanying the formation of TSC and TSDA complexes together with the values for the formation of the corresponding semicarbazide complexes. The high stability

TABLE 2

Thermodynamic functions for complex formation with thiosemicarbazide and thiosemicarbazide *N,N*-diacetic acid

(a) thiosemicarbazide complexes

Cu(II)	ΔG_1	-8.48 ± 0.05 (-5.55)	Hg(II)	ΔG_2	-31.2 (-16.1)
	ΔH_1	-9.8 ± 0.1 (-5.8)		ΔH_2	-35.3 (-16)
	ΔS_1	-4.8 ± 0.3 (-1)		ΔS_2	-13.7 $(+0.3)$
	ΔG_2	-16.08 ± 0.05 (9.63)		ΔG_3	-34.4 (-21.1)
	ΔH_2	-17.8 ± 0.1 (12.0)		ΔH_3	-39.9 (-18)
	ΔS_2	-5.7 ± 0.4 (-8)		ΔS_3	-18.1 $(+10.2)$

(b) thiosemicarbazide *N,N*-diacetic acid complexes

	Mn(II)	Co(II)	Ni(II)	Cu(II)	Zn(II)
ΔG	−2.8	−7.5	−8.2	−11.2	−8.1
	(−3.6)	(−8.2)	(−8.9)	(−11.7)	(−9.2)
ΔH	+7.2	+2.6	−0.8	− 2.6	+3.1
	(+3.2)	(+0.7)	(−1.1)	(− 0.5)	(−0.4)
ΔS	+33	+33	+24	+28	+37
	(+22)	(+29)	(+26)	(+37)	(+29)

ΔG, ΔH in kcal mol^{-1}, ΔS in cal mol^{-1} K^{-1}
Values in parentheses refer to complexes of the oxygen analogues of the ligands.

of TSC complexes of Hg(II) is seen to be due predominantly to a large enthalpy change. In fact the value of ΔH becomes more negative as the donor is changed from O to S to Se i.e. as the donor becomes softer [11]. This clearly reflects increasing Hg—X bond strength. On the other hand ΔS becomes more negative as the ligand donor atom becomes softer. Ahrland [13] has attributed this to the decreasing interaction between the ligand and the solvent. Normally too an increase in the number of attached ligands is accompanied by a more negative value of ΔS because of the loss of ligand translational entropy. It will be noted that in the case of the semicarbazide complexes of Hg(II) both ΔS_2 and ΔS_3 are positive and ΔS_3 is more positive than ΔS_2 which can be attributed to the formation of a chelate with the resultant displacement of twice as many water molecules from the primary coordination sphere of the metal ion as in the case of TSC.

The Cu(II) complexes of TSC also owe their high stability to large negative values of ΔH. It is interesting to note that the corresponding selenosemicarbazide complexes have even larger negative values of ΔH but are less stable because of the relatively large negative values of ΔS which accompany them.

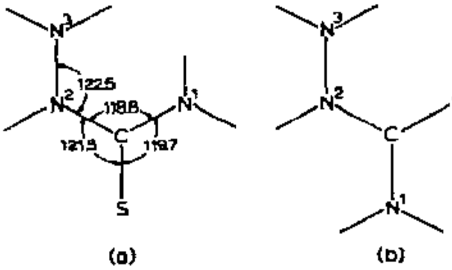
The stability of the TSDA complexes is mainly determined by the large positive ΔS values which accompany complex formation. This is due to the desolvation of the carboxylic acid groups which in the free ligand are extensively solvated. Nevertheless the ΔH values do show the relative affinity of the metal ions for sulphur. Thus only for Cu(II) and Ni(II) are the values of ΔH negative, and only for Cu(II) is the value of ΔH more negative for TSDA than for SDA.

Thus from the limited data available it is clear that TSC forms more stable complexes with soft or class (b) metal ions and as far as it is possible to tell this is due to larger enthalpy terms involved, i.e. the formation of stronger metal—ligand bonds.

C. X-RAY CRYSTALLOGRAPHIC DATA

It was only in 1969 that a full 3-dimensional crystal structure determination of thiosemicarbazide itself appeared in the literature [20], that is to say after much of the available data on TSC complexes had already been published*. The thiosemicarbazide molecule was found to be in the *trans* configuration (Fig. 1a), the arrangement of the non-hydrogen atoms being essentially planar.

However the only complexes so far known to contain TSC in this configuration are polymeric Ag(I) complexes. These are also the only known solid complexes in which TSC is monodentate and bonds through sulphur only [22—24]. In the polymeric complex, Ag(TSC)Cl, two kinds of silver atom are present, both being tetrahedrally coordinated but having environments which are both crystallographically and chemically distinct. Ag(I) is coordinated to two S atoms and two Cl atoms, with one of the Ag—Cl bonds longer than the other, while Ag(2) is coordinated to three S atoms and one Cl atom, with one of the Ag—S bonds being markedly longer than the other two [22] (Fig. 2). The silver coordination polyhedron in catena-μ-thiocyanato-bis(thiosemicarbazide) silver(I) is rather unusual, being a distorted trigonal pyramid involving two sulphur atoms from two TSC molecules, and one nitrogen and one sulphur from two different NCS groups (Fig. 3). The NCS groups are in bridging positions between two silver atoms, the bond through sulphur being



(a) (b)

Fig. 1. The structure of thiosemicarbazide (a) *trans* configuration as in the free ligand, (b) *cis* configuration as in its bidentate chelating form.

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* A preliminary report containing the essential molecular parameters was however published in 1966 [21].

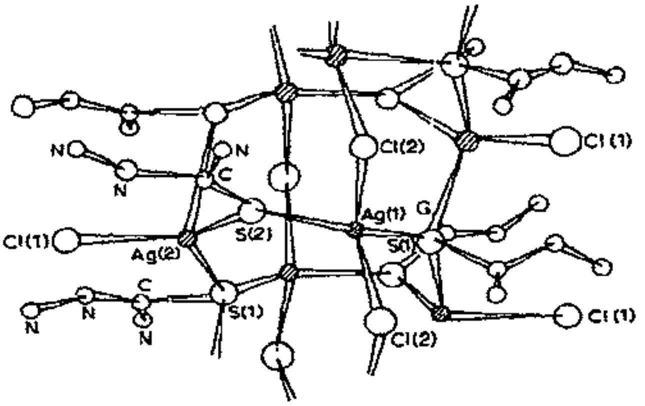

Fig. 2. The coordination polyhedra in Ag(TSC)Cl (hydrogen atoms not shown).

relatively weak, as shown by the rather long Ag—S distance of 2.99 Å. There are three longer contacts to two nitrogens and a sulphur which complete the coordination polyhedron to a distorted pentagonal bipyramid [23]. The structure of $Ag_2Br_2(TSC)_3$ involves tetrahedrally coordinated silver atoms distorted towards a trigonal pyramidal coordination, one bond being much longer than the others (Fig. 4). Pairs of non-equivalent polyhedra are joined together in dimers by the sharing of an S···S edge. The sulphur bridge which joins tetrahedra is of the same kind as those in bis(thiourea)silver(I) chloride and bis(thiourea)copper(I) chloride and has been interpreted as a 3-centre electron-deficient bridge bond [24].

In all other known TSC complexes the TSC molecule is in the *cis* configuration (Fig. 1(b)) and is bidentate, bonding through sulphur and hydrazinic nitro-

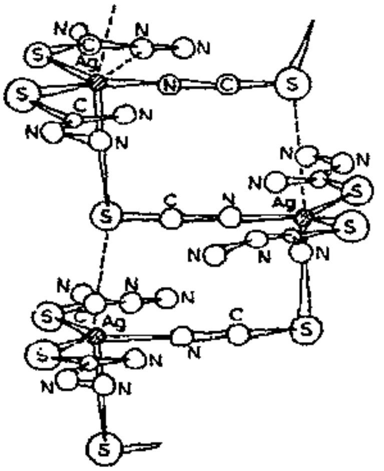

Fig. 3. The coordination polyhedra in *catena*-μ-thiocyanato-bis(thiosemicarbazide) silver(I) (hydrogen atoms not shown).

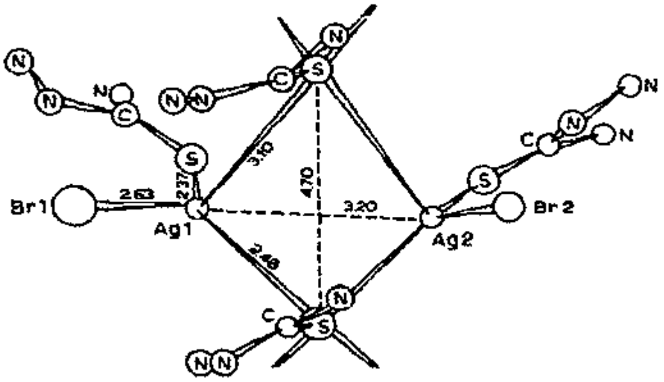

Fig. 4. The coordination polyhedra in $Ag_2Br_2(TSC)_3$ (hydrogen atoms not shown).

gen. The single crystal data available are somewhat limited (see Table 3) and five of the nine compounds studied which involve bidentate TSC contain nickel(II), three of them being square planar. $NiTSC_2SO_4$, $NiTSC_2SO_4 \cdot 3H_2O$ and $Ni(TSC-H)_2$ are all square planar and diamagnetic, and the Ni—N and Ni—S bond distances are very similar in all three compounds. The Ni—S bond distances are considerably shorter than the sum of the radii of the Ni(II) ion and the sulphur atom (2.4—2.5 Å) and also shorter than the sum of the Pauling covalent radii (2.25 Å). Thus there must be appreciable covalency in these bonds. The Ni—N bond distances are similar to those found in other square planar complexes with sp^3 hybridised nitrogen. The most interesting feature is the presence of both *cis* and *trans* isomers of the $Ni(TSC)_2^{2+}$ cation in the compound $Ni(TSC)_2SO_4$. When this work was first published [25] the occurrence of two isomers in the same structure was rather novel but since then other examples of this phenomenon have been reported [28]. The Ni—S bond is shorter in the *cis* isomer and Grønbaek argues [25] that this is due to the fact that S exerts a stronger *trans* effect than NH_2. It could equally well be taken as evidence of the importance of π-bonding in the Ni—S bond, but in fact this may amount to the same thing.

Although the Ni—N and Ni—S bond distances in $Ni(TSC-H)_2$ are similar to those in the two sulphate complexes, the bond angles about Ni deviate appreciably from 90° and there are marked changes in the geometry of the ligand [27]. The short C—N(2) distance shows this to be essentially a localised double bond, implying that the ligand is in the thiol form (Fig. 5) which has been deprotonated. There is other evidence that this is the form involved in complex formation under alkaline conditions. Nardelli and co-workers [20] have pointed out that in TSC itself the C—S and C—N(1) bond distances are intermediate between the usual values for single and double bonds. It is therefore interesting to note that in $Ni(TSC-H)_2$ these bonds and also the N(2)—N(3) bond are markedly longer than in TSC while, as noted above, the C—N(2) bond is appreciably shorter. This appears to be the only structure in which this essentially localised form of the bonds in the TSC fragment has been found.

TABLE 3

Crystallographic data for complexes of thiosemicarbazide and thiosemicarbazones

Compound	Space group	Z	R%	M–S	M–N	SMN	C–S	C–N^1	C–N^2	N^2–N^3	Other data	Ref.
TSC (free ligand)	$P\bar{1}$	2	9.9				1.685	1.313	1.337	1.399		20, 21
$NiTSC_2SO_4$	*Aa* or *A*2/*a*	8	5	2.149 2.169	1.930 1.926	89.14 89.10	1.731 1.721	1.331 1.323	1.336 1.327	1.428 1.431	*cis* *trans*	25
$NiTSC_2SO_4 \cdot 3H_2O$	$P2_1/m$	2	9.2	2.16	1.90	89.97	1.75	1.29	1.33	1.44	Ni—O 3.98	26
$Ni(TSC\text{-}H)_2$	$P2_1/c$	2	12.6	2.155	1.911	81.7	1.746	1.436	1.247	1.537		27
$NiTSC_2(NO_3)_2 \cdot 2H_2O$	$P\bar{1}$	1	6	2.411	2.059	83.95	1.694	1.330	1.338	1.416	Ni—O 2.123	29
$NiTSC_3(NO_3)_2 \cdot H_2O$	$Pna2_1$			2.45								29
$FeTSC_2SO_4$	$I2/a$	8	4.6	2.425 2.427	2.195 2.164	81.0 81.3					*cis* Fe—O 2.165 *trans* Fe—O 2.187	28(b)
$CuTSC_2SO_4$	$P\bar{1}$	2	6.3	2.259 2.266	2.031 2.031	86.4 85.9	1.706 1.723	1.304 1.306	1.350 1.323	1.415 1.406	Cu—O 2.34	30
$CuTSC_2(NO_3)_2$	$P\bar{1}$	1	6.4	2.286	2.001	86.2	1.713	1.315	1.330	1.411	Cu—O 2.773	31
$Zn(TSC)Cl_2$	*Pnma* or $Pn2_1a$	8	11.4	2.286 2.298	2.11 2.08	89.1 90.5	1.73 1.72	1.29 1.27	1.28 1.27	1.44 1.40	Zn—Cl 2.238 (I) Zn—Cl 2.247 (II) ClZnCl 106.3 (I) ClZnCl 110.7 (II) ClZnS 115.6 (I) ClZnS 121.8 (II)	32
Ag(TSC)Cl	$P2_12_12_1$	8	10.5	2.51 Ag(I)[a] 2.50 Ag(I)							Ag—Cl 2.65 (I) Ag—Cl 2.75 (I)	22
			10.5	2.51 Ag(II) 2.48 2.77							Ag—Cl 2.66 (II)	22
$Ag(TSC)_2NCS$	$Pna2_1$	4	14	2.43 2.48 2.99 Ag—SCN(I) 3.63 Ag—SCN(II)	3.42 Ag—N^1 3.30						Ag—N 2.24 (Ag—NCS)	23

				2.37 Ag(I)—S(II) 2.49 Ag(II)—S(I) 2.36 Ag(II)—S(III) 3.10 Ag(I′)—S(I) 3.05 Ag(II′)—S(I)							Ag(II)—Br 2.71	
TSCAC							1.690	1.334	1.342	1.398		38
NiTSCAC$_2$Cl$_2$·H$_2$O	$Pca2_1$		4.7	2.291	2.136	88	1.728	1.301	1.323	1.382	Ni—Cl 2.305	35
				2.315	2.128		1.710	1.335	1.336	1.395	C=N 1.274, 1.265	
NiTSCAC$_2$(NO$_3$)$_2$				2.335	2.180		1.645	1.379	1.353	1.392	C=N 1.312	36
				2.310	2.118		1.739	1.285	1.382	1.446	C=N 1.303 Ni—O 2.114, 2.223	
Zn(TSCAC)Cl$_2$	$P2_1/n$	4	4.5	2.303	2.116	85.2	1.712	1.313	1.332	1.392	C=N 1.292 [a] Zn—Cl 2.252 Zn—Cl 2.203	33
Ni(TSC-2,5-D-2H)	$P2_1/c$	4	10	2.16	1.91	84	1.76	1.38	1.31	1.41	C=N 1.33 [b]	34
				2.18	1.98	86	1.76	1.38	1.30	1.40	C=N 1.30	
Ni(TSCPHAL-2H)	$P2_12_12_1$	4	10	2.16	1.92	88	1.72	1.35	1.35	1.41	C=N 1.33 [b]	34
				2.17	1.93	88	1.74	1.36	1.32	1.41	C=N 1.33	
KTS	$P2_1/c$	2		TSC moiety 1			1.689	1.314	1.351	1.379	C=N 1.284 (I)	40
				TSC moiety 2			1.682	1.311	1.352	1.365	C=N 1.290	
				TSC moiety 1			1.692	1.310	1.351	1.371	C=N 1.285 (II)	
				TSC moiety 2			1.687	1.305	1.359	1.371	C=N 1.294	
Cu(KTS)	[c]			2.26	1.98	84	1.76	1.33	1.33	1.34	C=N 1.30	39
				2.27	1.97	84	1.74	1.36	1.32	1.35	C=N 1.29	
Ni(1-FIQTSC)$_2$	$C2/c$	8	4.5	2.412	2.026 2.114 Ni—N (ring)	81.3	1.719	1.345	1.331	1.357	C=N 1.279 (I)	37
				2.425	2.013 2.110 Ni—N (ring)	81.1	1.735	1.350	1.328	1.356	C=N 1.295 (II)	
Ni(2-FPYTSC)$_2$				2.410	2.055 2.106 Ni—N (ring)	80.7	1.725	1.352	1.308	1.370	C=N 1.260 (I)	38
				2.440	2.056 2.125 Ni—N (ring)	79.3	1.740	1.336	1.326	1.342	C=N 1.285 (II)	

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[a] C=N refers to the carbonyl carbon to hydrazine nitrogen bond in thiosemicarbazones. [b] The authors of ref. 34, who kindly supplied data prior to publication, wish to stress that these are not final geometries. [c] Reference 39 contains no mention of the space group, Z, or the value of R. [d] Roman numbers in parentheses, e.g. (I), refer to crystallographically different units and not to oxidation numbers.

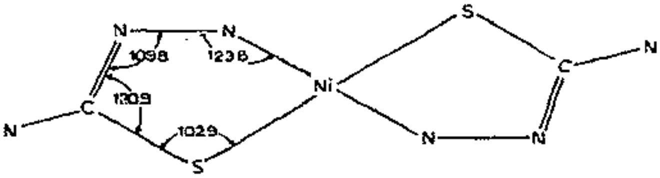


Fig. 5. The molecular structure of $Ni(TSC\text{-}H)_2$ (hydrogen atoms not shown).

It would be interesting to see if other TSC—H complexes contain the same localised bond system. In the nickel sulphate complexes the C—N(1) and C—N(2) bond distances are not very different from those in TSC itself while the C—S and N(2)—N(3) distances are longer as might be expected for bonds involving donor atoms.

In the paramagnetic 6-coordinate complex $NiTSC_2(H_2O)_2(NO_3)_2$ the coordination about Ni is approximately octahedral with two O, two N and two S atoms in *trans* positions relative to each other. The Ni—N and Ni—S bonds are much longer than in the diamagnetic complexes but the ligand geometry is much the same as in TSC itself. The Ni—S bond length is in the lower end of the range 2.4—2.6 Å generally accepted for octahedral Ni(II) molecules. The Ni—N distances also lie in the range usually found for octahedral Ni(II) complexes [29].

The crystal structure of $FeTSC_2SO_4$ is very interesting as it consists of a chain-like polymer in which SO_4 ions act as bridges between *cis* and *trans* $FeTSC_2$ units [28b] (Fig. 6). It is worth noting that not only are the Fe—S distances in the two isomeric units identical but they are among the longest Fe—S distances known. Thus in this case π-bonding in the metal sulphur bond

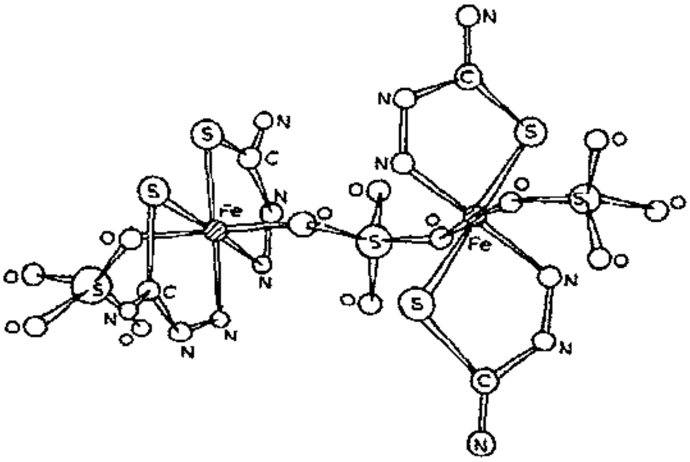


Fig. 6. Part of the polymeric chain in the structure of $FeTSC_2SO_4$ showing the two kinds of iron(II) atom present (hydrogen atoms not shown).

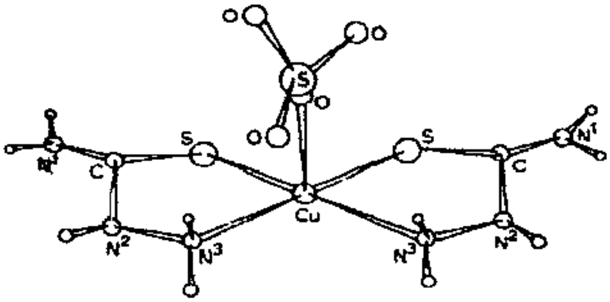


Fig. 7. The molecular structure of $CuTSC_2SO_4$.

can be ruled out. On the other hand the Fe—O distances are remarkably short being of the same order as the Fe—N distances (see Table 3). An interesting point is that the Fe—O distance in the *trans* unit and the Fe—N distance in the *cis* unit are equal. It must be noted that there are appreciable distortions from octahedral symmetry in both isomeric units, the SFeN angles being ca. 81° and the OFeO angles being ca. 173°.

Two copper(II) complexes of TSC have been studied by single crystal methods, $CuTSC_2SO_4$ and $CuTSC_2(NO_3)_2$ [30, 31]. In the sulphate the copper atom is pentacoordinate and the TSC molecules are bonded in a *cis* configuration, the two sulphur and two hydrazinic nitrogen atoms forming the corners of the base of a square pyramid (Fig. 7). The apex of the pyramid is occupied by an oxygen atom of the sulphate group which behaves as a monodentate ligand [30]. The Cu—O bond is relatively short (2.34 Å) showing that this bond is quite strong. In the nitrate, on the other hand, the copper atom is in a tetragonal environment [31]. The two TSC molecules are chelated in a *trans* configuration to give a near-planar grouping, the 6-coordination being completed by two oxygen atoms from the two *trans* nitrate groups. The nitrate groups are relatively weakly bonded to copper as is shown by the fact that coordination does not alter the N—O distances in the NO_3 group as well as by the long Cu—O bond (2.773 Å). It is interesting to note that in the sulphate with its *cis* grouping of the TSC molecules the Cu—S bond is shorter and the Cu—N bond longer than in the nitrate with its *trans* grouping of the TSC molecules, the geometry of the ligand being much the same in both compounds. As in the case of the nickel(II) compounds (see above) this can be explained either by the importance of π-bonding in the Cu—S bond or by the stronger *trans* effect of S.

In $Zn(TSC)Cl_2$ the Zn atom is tetrahedrally coordinated to two Cl atoms and one TSC molecule, the Zn atom lying in the plane of the TSC molecule (Fig. 8). The Zn—N and Zn—Cl bond distances lie in the range expected for tetrahedral zinc molecules, while the Zn—S bond length constitutes the lower limit of the range found for the limited number of compounds containing Zn—S bonds which have been studied. The geometry of the TSC moiety is somewhat changed compared with TSC itself, the C—S and N(2)—N(3) bonds

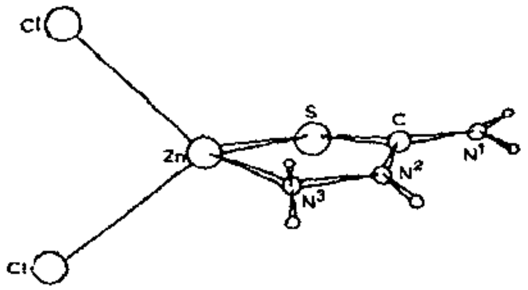


Fig. 8. The molecular structure of $Zn(TSC)Cl_2$.

being longer and the C—N(1) and C—N(2) bonds being shorter. The NZnS angle is about 90° instead of the theoretical 109° and the CN(2)N(3) angle has opened to about 132° (note that there are two crystallographically different groups of molecules in the unit cell with slightly different parameters) [32]. If we compare these data with those for the corresponding acetone thiosemicarbazone (TSCAC) complex, $Zn(TSCAC)Cl_2$, we find that the Zn—N and Zn—S distances are much the same in the two compounds, while the Zn—Cl distances in $Zn(TSCAC)Cl_2$ are significantly different both from each other and from the distances in $Zn(TSC)Cl_2$. In the TSCAC complex one of the Cl atoms is involved in hydrogen bonding but the other is not. More important the Zn atom is displaced from the plane of the organic ligand by 0.433 Å with the result that the internal geometry of the TSCAC ligand is very similar to that of the free ligand [33].

Of the eight thiosemicarbazone complexes whose structures have been determined six contain nickel(II). McCleverty and co-workers [34] have determined the structures of the two square planar diamagnetic complexes formed with the bisthiosemicarbazones of hexene-2,5-dione (TSC—2,5-D) and phthalaldehyde (TSCPHAL). Both of the complexes contain a seven-membered chelate ring as well as the two five-membered rings involving the TSC moieties. Although no information is available on the geometries of the free ligands, so that a really meaningful comparison is not possible, it is worth noting that the C—S and N(2)—N(3) as well as the Ni—N and Ni—S bond lengths are similar to those found in the square planar nickel(II) complexes of TSC. In Ni(TSC-2,5-D-2H), (Fig. 9(a)), the coordination about the Ni atom involves a distortion from square planarity such that the Ni, the two S and one of the coordinated nitrogens are approximately coplanar, while the other coordinated nitrogen is 0.66 Å from this mean plane. On the other hand in Ni(TSCPHAL-2H), (Fig. 9(b)), the coordination about Ni is substantially planar but the two TSC chelate planes are mutually inclined at an angle of 33° and are symmetrically oriented with respect to the mean coordination plane of the nickel.

In the complex $Ni(TSCAC)_2Cl_2$ the Ni atom is pentacoordinated with the donor atom set N_2S_2Cl, the two S atoms being in the axial positions of an approximately trigonal bipyramidal coordination polyhedron. The geometries

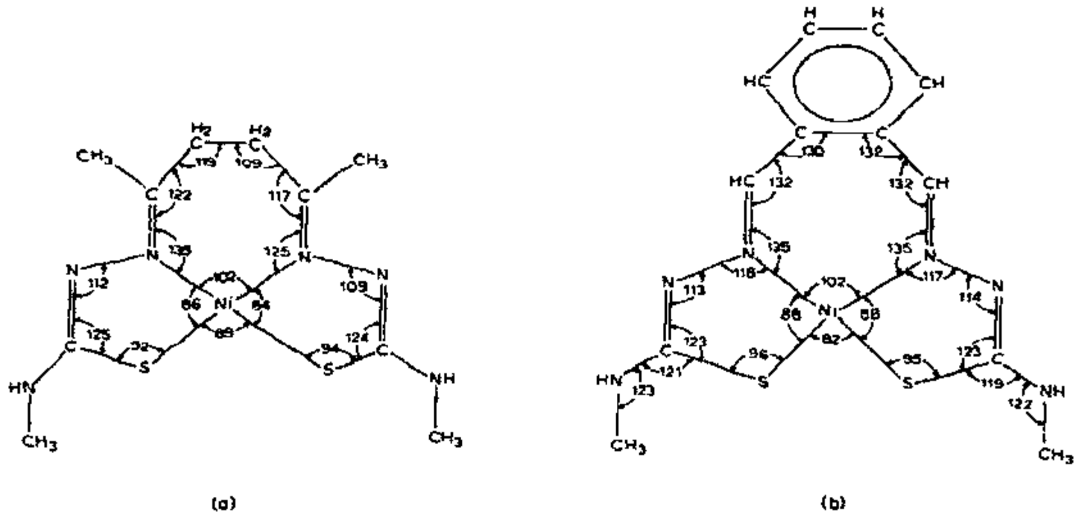


Fig. 9. Schematic molecular structures of the square planar nickel(II) complexes with (a) hexene-2,5-dione bis(thiosemicarbazone) and (b) phthalaldehyde bis(thiosemicarbazone).

of the two TSCAC ligands are not identical but apart from the longer C—S bond lengths they are not very different from that of the free ligand. The Ni—S bond lengths are intermediate between those found for 4- and 6-coordinated nickel(II) complexes of thiosemicarbazones (see Table 3), as might have been expected, but the Ni—N distances are longer than those in both 4- and 6-coordinated species [35]. In the corresponding nitrate complex, $Ni(TSCAC)_2(NO_3)_2$, the Ni atom is 6-coordinate with the donor atom set $N_2S_2O_2$ but only one of the NO_3 groups is coordinated and is therefore necessarily bidentate (Fig. 10). However the coordination polyhedron is distorted

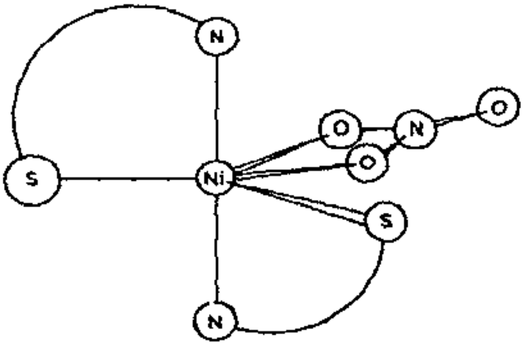
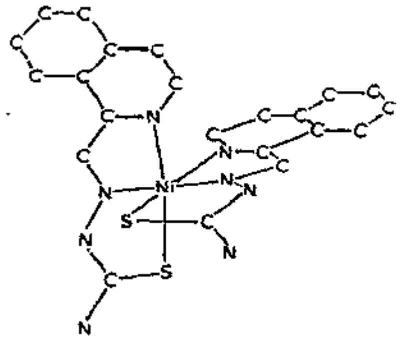
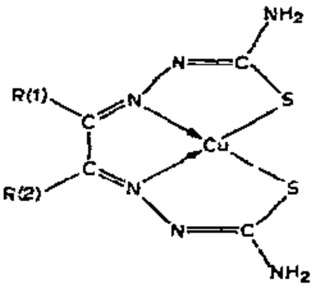


Fig. 10. Schematic molecular structure of the nitrato bis(acetone thiosemicarbazone) nickel(II) cation (only the N and S donor atoms of the thiosemicarbazone ligands are shown).





(For Cu(KTS) R(1) = H, R(2) = $CH(CH_3)OCH_2CH_3$)

Fig. 11. Schematic molecular structure of bis(isoquinoline-1-carboxaldehyde thiosemicarbazanato) nickel(II) monohydrate (hydrogen atoms not shown).

Fig. 12. Schematic molecular structure of the square planar Cu(KTS) molecule.

towards an approximately trigonal bipyramidal shape, with the coordinated bidentate NO_3 effectively occupying a single coordination position. The two Ni—O bond lengths are appreciably different as are the Ni—S and especially the Ni—N bond lengths [36].

The structures of two 6-coordinate complexes of Ni(II) with thiosemicarbazones have been determined and these must almost certainly be paramagnetic. The ligands are the thiosemicarbazones of 1-formaldehyde isoquinoline and 2-formaldehyde pyridine, TSCFIQ and TSCFPY, which are tridentate, the third donor atom being the heterocyclic nitrogen. Because of the coplanarity of the three ligand donor atoms, NNS, the two S atoms are necessarily *cis*. In each case there are significant differences in the parameters found for the two ligand molecules in the complex [37, 38]. The Ni—S bond lengths are appreciably longer than those in the 4- and 5-coordinate complexes and are similar to the values found for the paramagnetic 6-coordinate nickel(II) complexes of TSC (see Table 3). The Ni—N (hydrazinic N) bond lengths are intermediate between those in the 4- and 5-coordinate species and are appreciably shorter than the Ni—N (heterocyclic N) bond lengths (Fig. 11).

The observations of Petering and co-workers [10] that the active species in anti-tumour activity of 3-ethoxybutane-1,2-dione bis-thiosemicarbazone (H_2KTS) was the copper(II) chelate Cu(KTS) were soon followed by the publication of the crystal structure of the chelate [39] (Fig. 12). The two TSC moieties in the ligand are necessarily in a *cis* position to each other and it is interesting to note that the Cu—S bond distances (see Table 3) are very similar to those found in $Cu(TSC)_2SO_4$ which also has the TSC moieties in a *cis* configuration (see above). However it is also worth noting that the Cu—N bond distances in Cu(KTS) are appreciably shorter than those in $Cu(TSC)_2SO_4$ and that furthermore the geometries of the two TSC residues in the former compound show a marked tendency towards bond delocalisation. Thus the C—N(1), C—N(2) and N(2)—N(3) bond lengths are very similar and the N(2)—N(3) bond is exceptionally short. Although the structure of the free ligand H_2KTS has been determined [40], comparison with the geometry of the ligand in the chelate is fairly meaningless, both because the chelate contains the ligand in a deprotonated form which necessarily involves changes in bond lengths and bond angles (cf. TSC and TSC—H in $Ni(TSC\text{-}H)_2$), and because the free ligand is in an extended configuration.

TABLE 4

Room temperature magnetic moments for some thiosemicarbazide and thiosemicarbazone complexes

Complex	μ_{eff}^{a}	Ref.	Complex	μ_{eff}	Ref.
(i) Thiosemicarbazide complexes					
$Cu(TSC)Cl_2$	1.74 [b]	41	$FeTSC_2SO_4$	5.49	43
$Cu(TSC)Br_2$	1.67 [b]	41	$NiTSC_2(NO_3)_2\cdot 2H_2O$	3.19	44
$CuTSC_2Cl_2$	1.77	42	$NiTSC_2(ClO_4)_2\cdot 3H_2O$	3.15	46
$CuTSC_2Br_2$	1.78	42	$NiTSC_2(NCS)_2$	3.15	46
$CuTSC_2(NO_3)_2$	1.80	42	$NiTSC_2(NO_2)_2$	2.99	46
$CuTSC_2(ClO_4)_2$	1.83	42	$NiTSC_3Cl_2\cdot 3H_2O$	3.05	44
$CuTSC_2SO_4$	1.64	42	$Ni(4EtTSC)_3SO_4$	3.07	44
(ii) Thiosemicarbazone complexes					
$Ni(2PATSC)_2Cl_2\cdot H_2O$	3.27	47	$NH_4Fe(SALTSC\text{-}2H)_2$	2.50	69
$Ni(2PATSC\text{-}H)_2\cdot \frac{1}{2}H_2O$	3.19	47	$Fe(SALTSC\text{-}H)Cl_2\cdot 2\frac{1}{2}H_2O$	6.00	69
$Co(ISTSC\text{-}H)_2\cdot 2H_2O$	5.06	48	$Fe(SALTSC\text{-}H)Br_2\cdot 2\frac{1}{2}H_2O$	5.98	69
$Ni(ISTSC\text{-}H)_2$	3.12	45	$Fe(MePVTSC\text{-}H)_2$	5.08	69
$Cu(ISTSC\text{-}H)Cl$	1.81 [c]	45	$Co(8QATSC)_2Cl_2\cdot 3H_2O$	4.42	52
$Ni(MeISTSC\text{-}H)_2$	3.8	45	$Co(8QATSC)_2SO_4\cdot 6H_2O$	4.35	52
$Cu(MeISTSC\text{-}H)Cl$	1.81 [c]	45	$Ni(8QATSC)_2Cl_2\cdot 3H_2O$	2.99	53
$Co(PVATSC\text{-}H)_2\cdot H_2O$	4.59	50	$Ni(8QATSC)_2SO_4\cdot 6H_2O$	3.05	53
$Ni(PVATSC\text{-}H)_2\cdot H_2O$	3.05	50	$Ni(8QATSC\text{-}H)_2\cdot 4H_2O$	3.04	53
$Ni(PVATSC\text{-}2H)\cdot py$	0	50	$Ni(8QATSC)Cl_2\cdot 3\frac{1}{2}H_2O$	3.07	53
$Cu(PVATSC\text{-}H)\cdot 2H_2O$	1.77	49	$Ni(8QATSC\text{-}H)NCS$	0	53
$Cr(PVATSC\text{-}H)_2$	3.10	51	$Ni(TSCAC)_2Cl_2\cdot H_2O$	3.29	54a
$NH_4Cr(PVATSC\text{-}2H)_2$	3.76	51	$Ni(TSCAC)_2Br_2\cdot H_2O$	3.00	54a
$NH_4Fe(PVATSC\text{-}2H)_2$	2.02	51	$Ni(CHTSC)_2Cl_2$	3.34	54a
$Fe(PVATSC\text{-}H)_2\cdot H_2O$	5.18	51	$Ni(CHTSC)_2Br_2$	3.20	54a

[a] In μ_B. [b] Studied over the range 373.2 to 80.4 and 303.2 to 88.4 K respectively, these compounds have $2J$ values of -6 and -24 cm^{-1} and θ values of 0 and -24 K. [c] These compounds were studied over the range 296 to 77 K and have θ values of $+10°$ and $24°$K respectively.

D. MAGNETIC DATA

(i) Magnetic susceptibility

(a) Thiosemicarbazide complexes

The room temperature magnetic moments of some TSC complexes are shown in Table 4. The only TSC complexes which have been studied over a temperature range are $Cu(TSC)Cl_2$ and $Cu(TSC)Br_2$ in which bridging by both halogen and TSC leads to weak anti-ferromagnetism [41]. It is unfortunate that no thorough study of a complex in which TSC is the only ligand has been made since a knowledge of the reduction parameters would give an insight into the covalency of the metal—sulphur bond. However such a study has been made using EPR and the copper—sulphur and the copper—nitrogen bonds in $CuTSC_2^{2+}$ have been shown to be highly covalent [60] (see Section D(II)).

(b) Thiosemicarbazone complexes

Again only two thiosemicarbazone complexes have been studied over a temperature range, Cu(ISTSC-H)Cl and Cu(MeISTSC-H)Cl [45]. Unfortunately although these compounds are said to be antiferromagnetic the *J* values are not reported. The authors exclude a halogen bridged structure because of the relatively small variation of susceptibility with temperature and also because the value of ν(Cu—Cl) would seem to indicate a terminal halogen.

However even room temperature moments do often prove useful in assigning the stereochemistry about the metal ion and hence the probable coordinating behaviour of the ligand. Thus the paramagnetism of $Ni(ISTSC\text{-}H)_2$ (see Table 4) with μ_{eff} = 3.12 BM at 296 K lies in the range expected for octahedrally coordinated Ni(II) which suggests that the ligand is probably terdentate with the ketone oxygen acting as a donor as well as the N and S of the TSC residue. Similarly the relatively high value of the magnetic moment of $Ni(MeISTSC\text{-}H)_2$, 3.8 BM at 296 K, suggests that the Ni(II) ion is tetrahedrally coordinated so that the ligand here must be bidentate. Similarly the magnetic moment data in Table 4 show the ligands PVATSC and 8QATSC to be terdentate in the complexes studied.

(ii) EPR spectra

The spin Hamiltonian parameters for the *trans* $CuTSC_2^{2+}$ ion have been obtained from a Q-band EPR study of the Cu(II) ion doped in $NiTSC_2SO_4 \cdot 3H_2O$ at a concentration of ca. 2%. The data obtained are shown in Table 5. Assuming that the Cu(II) ion substitutes for Ni(II) the environment of the copper atom will be *trans* square planar N_2S_2. The shortest metal—oxygen distance in the host crystal is 3.98 Å (see Table 3, ref. 26) and it is therefore reasonable to assume that oxygen does not contribute to the bonding. From

TABLE 5

(i) EPR parameters for copper(II) complexes

Complex	g values	A values (10^4 cm^{-1})	A^N values (10^4 cm^{-1})	Ref.
Ni(^{63,65}Cu)TSC$_2$SO$_4$·3H$_2$O	g_x 2.023 g_y 2.041 g_z 2.127	A_x 33.05 A_y 45.34 A_z 186.6 (^{63}Cu) A_z 196.4 (^{65}Cu)	$A_{z'}$ 16.71 $A_{x'} = A_{y'} = 14.33$	55
Zn(^{63}Cu)TSC$_2$SO$_4$	g_x 2.028 g_y 2.045 g_z 2.159	A_x 32.1 A_y 44.6 A_z 186.0	$A_{z'}$ 10.5 $A_{x'} = A_{y'} = 9.6$	56
CuTSC$_2$(ClO$_4$) in DMF	g_1 2.025 g_2 2.045 g_3 2.152	A_1 21.0 A_2 25.0 A_3 186.6	$A_{z'}$ 12.8 $A_{x'} = A_{y'} = 10.0$	56
CuTSC$_2$(ClO$_4$)$_2$ in ETG/H$_2$O	g_1 g_2 g_3			56
CuKTS polycrystalline	$g_\parallel$ 2.12	$g_\perp$ 2.03		62
CuKTS in DMF	$g_\parallel$ 2.14 $g_\perp$ 2.02	$A_\parallel$ 186.8 $A_\perp$ —[a]	A^N 11.0	62
CuKTS dimer in 30% dioxane in ethanol	$g_\parallel$ 2.16 $g_\perp$ 2.03	$A_\parallel$ 90 $A_\perp$ —[a]		62
Cu(DDTSC-H)$_2$ 1% in nickel(II) salt also in DMF (see text)	$g_\parallel$ 2.12 $g_\perp$ 2.00	$A_\parallel$ 190.5 $A_\perp$ 34.7	A^N 14.8—14.0	66
CuBUTSC$_2^{2+}$ in DMF	$g_\parallel$ 2.15 $g_\perp$ 2.04	$A_\parallel$ 150 $A_\perp$ —[a]	$A^N < 8$	62
Cu(BUTSC-H)$_2$	$g_\parallel$ 2.14 $g_\perp$ 2.02	$A_\parallel$ 186.8 $A_\perp$ —[a]	A^N 15	62
CuTSC$_2$(NO$_3$)$_2$	g_1 2.0269 g_2 2.0474 g_3 2.1525			55

[a] Not reported.

(ii) Covalency parameters

Complex					
Ni(^{63,65}Cu)TSC$_2$SO$_4$·3H$_2$O	α^2 0.68 β_1 0.71	γ_N^2 0.16 β_N 0.81	γ_S^2 0.33 β_S 0.75	ξ — 0.038	for n_S $(\frac{2}{3})^{1/2}$
	α^2 0.72 β_1 0.77	γ_N^2 0.16 β_N 0.80	γ_S^2 0.27 β_S 0.89	ξ — 0.027	for n_S (1)
	α^2 0.70 β_1 0.76	γ_N^2 0.16 β_N 0.81	γ_S^2 0.33 β_S 0.70	ξ — 0.031	for n_S $(\frac{2}{3})^{1/2}$
	α^2 0.73 β_1 0.81	γ_N^2 0.11 β_N 0.79	γ_S^2 0.26 β_S 0.65	ξ — 0.033	for n_S (1)
Zn(^{63}Cu)TSC$_2$SO$_4$					

α, γ_N and γ_S are the metal, N and S coefficients in the σ-bonding MO, ξ is the mixing coefficient for the d_z^2 metal orbital in the σ-bonding MO, β_1, β_N and β_S are the metal orbital coefficients in the in-plane and the two out-of-plane bonding MOs.

the observed g values it is clear that the ground state is essentially $d_{x^2-y^2}$ although because of the low effective symmetry (D_{2h}), there will be some mixing in of the d_{z^2} orbital into the ground state. It is significant that the g values are smaller than those found for CuN_4 chromophores [57, 58] but are close to those found for CuS_4 chromophores [59]. This alone would suggest that there must be considerable covalency in the bonds. There is also the fact that the unpaired electron interacts strongly with the two coordinated nitrogen atoms giving rise to a well resolved five-line ligand hyperfine structure in the EPR spectrum, the very narrow lines being only a few gauss wide [55]. The bonding parameters which are shown in Table 5 were evaluated on the basis of an LCAO—MO scheme using the EPR parameters and optical data obtained from a single crystal study of $CuTSC_2(NO_3)_2$ [60]. It will be noticed that both the Cu—N and Cu—S bonds are highly covalent. The Cu—S bonds are probably the most covalent copper-ligand bonds yet known. It is interesting to note the strong anisotropy in the covalency of the ground state A_g orbital, the Cu—S being about twice as covalent as the Cu—N bond. The value of γ_S^2 (ca. 0.30) is similar to values found for bis(dithiocarbamato) copper(II) complexes [59]. The percentage electron density at the nitrogen atoms, derived directly from the ligand hyperfine coupling constants, is comparable to that found in strongly covalent copper(II) complexes containing only nitrogen donor atoms [58]. It is also worth noticing that there is appreciable covalency in the out-of-plane π-bonds between both Cu and S and Cu and N, and that contrary to suggestions made in the case of bis(dithiocarbamato) copper(II) complexes [59], the in-plane π-covalence is not negligible.

Accurate values of the three principal g values of $CuTSC_2(NO_3)_2$ have been obtained from powder spectra of the undiluted compound both at Q-band and at X-band frequencies [55, 56]. The values of g_1 and g_2 (see Table 5) are in good agreement with the values of g_x and g_y found for the diluted sulphate, while the difference between g_3 and g_z is the result of different amounts of axial (z-axis) coordination in the two compounds. It is well known that an increase in the field along the z-axis is accompanied by an increase in the value of g_z. Smith has pointed out [61] that stronger axial bonding leads to an increase in the length of the bonds in the xy-plane which results in a decrease of both the in-plane covalency and the energy of the $d_{x^2-y^2}$—d_{xy} transition. Both of these effects are factors which tend to increase the value of g_z. In order to determine the relative importance of these factors experimentally an X-band EPR study of the $^{63}Cu(II)$ ion doped in $ZnTSC_2SO_4$, at a concentration of ca. 2%, has been made [56]. The IR and electronic spectra of the doped crystals show that the environment of the Cu(II) ion in this host is tetragonal rather than square planar due to an axial interaction with the SO_4 groups. The spin Hamiltonian parameters are shown in Table 5 and it will be noticed that the g values are similar to those of $CuTSC_2(NO_3)_2$. The decrease in the value of A_z, compared with its value in the nickel doped sample, is to be expected in view of the anticipated increase in the amount of d_{z^2} character in the ground state. The marked decrease in the values of the ligand hyperfine coupling constants is the expected result of an increase in the length of the bonds in the xy-plane. It is worth noting that very similar g and A values are obtained from analysis of the frozen solution spectra of $CuTSC_2(ClO_4)_2$ in DMF and ethylene glycol/water mixtures [56].

The complex Cu(KTS) is of particular interest because of its marked antitumour activity in rats [10]. Blumberg and Peisach [62] have studied the X-band EPR spectrum of this compound in DMF at 1.4 K. Unfortunately the sample they used contained isotopically normal copper (69% ^{63}Cu, 31% ^{65}Cu) with the result that anomalous lines appeared in the ligand hyperfine structure because of the non-coincidence of the two sets of lines arising from the two copper isotopes. This was undoubtedly compounded by considerable g anisotropy similar to that found for the TSC complexes above. As a result they erroneously interpreted the ^{14}N hyperfine structure as arising from the interaction of the unpaired spin with four equivalent ^{14}N nuclei which, since the crystal structure [39] shows copper to be coordinated to only two N and two S atoms, would imply a high degree of delocalisation in the chelate rings. While this seems an attractive idea, especially as the bond lengths in the TSC moieties do indicate intermediate bond order [39] (see Table 3), subsequent work on other bis(thiosemicarbazone) copper(II) complexes suggests it to be incorrect [63, 64].

Thus Hatfield and co-workers [63] examined the solution spectra of two analogous compounds (see Fig. 12, I $R(1) = R(2) = CH_3$, II $R(1) = CH_3$, $R(2) = C_5H_{11}$) which had been prepared from pure ^{63}Cu. They found that the ^{14}N ligand hyperfine structure superimposed on each of the copper hyperfine lines consisted of only five lines showing that the unpaired spin interacts with only two nitrogen nuclei. Similarly Getz and Silver [64] examined the X-band spectrum of Cu(II) doped into the diamagnetic nickel(II) analogue of Hatfield's compound I (Fig. 13, $R(1) = R(2) = CH_3$) and they also found a five line ^{14}N superhyperfine structure. Thus the degree of delocalisation in the chelate rings must be small and is obviously not sufficient to lead to a significant amount of unpaired electron density on N^2 (see Fig. 1).

Smith and co-workers [65] have also examined Hatfield's compound I in solution. They report that in DMSO at room temperature only monomeric species are formed while in the frozen solution at 77 K the $\Delta M = 1$ transition is broadened and a "$\Delta M = 2$" transition is observed providing clear evidence for dimer formation. They appear to have been interested only in the dimer species and do not report parameters for the monomer species. The copper—copper distance in the dimer was calculated to be 5.6 ± 0.5 Å. The value of $g_\parallel$ reported is markedly different from the values found for other compounds containing the TSC skeleton (see Table 5) and this may be the result of a real difference in the nature of the bonding. One possibility is that the ligand is in the protonated form. However the structure proposed by the authors seems rather improbable.

Hatfield and co-workers [66] examined the frozen solution spectra of compounds I and II as well as those of several other analogous bis(thiosemicarbazones). They found that the spectra of all these complexes were essentially identical. Furthermore for dilute solutions in DMF they did not report any evidence of dimer formation cf. Smith and co-workers [65] above. The parameters found by Hatfield and co-workers [66] are shown in Table 5 and it must be stressed that these were obtained from the spectrum of a sample which contained only ^{63}Cu. However Hatfield also examined solid solutions of compound I in its diamagnetic nickel(II) analogue. A 5% solid solution showed line broadening of the $\Delta M = 1$ transition and the spectrum also showed a half-field feature corresponding to the $\Delta M = 2$ transition of a species with $S = 1$, i.e. a dimer. The zero field splitting of the dimer species was calculated to be 0.014 cm^{-1}. The exchange coupling constant J was found to be approximately 22 cm^{-1} which is in qualitative agreement with the value of -14 cm^{-1} found by magnetic susceptibility measurements. The exchange coupling was believed to arise in the same way as in Cu(KTS) where pairs of planar molecules in the unit cell are related by an inversion centre with an axial Cu—S internuclear distance of 3.102 Å [39].

The EPR spectrum of red solid Cu(KTS) itself was studied by Blumberg and Peisach [62] who reported a strong exchange interaction with a singlet state ($S = 0$) lying lowest. From their data they calculated the singlet-triplet separation to be 23 K. They too attributed the coupling to the presence of the weak axial Cu—S bonds. They also reported that addition of acid to red Cu(KTS) gave a yellow species of the same formula which they assumed to be the protonated form. A concentrated solution of this species in DMF showed no EPR signal up to 130 K. To account for this they proposed a dimer structure in which the ligand is in an extended configuration similar to that found in crystalline KTS itself [40] (see Fig. 13).

The reaction of the copper(II) ion with alkyl mono-thiosemicarbazones normally leads at room temperature to the formation of a copper(I) thiosemicarbazone complex. However Blumberg and Peisach [62] succeeded in obtaining the EPR spectra of two copper(II) complexes with butyraldehyde thiosemicarbazone (BUTSC) by mixing the reactants quickly and then lowering

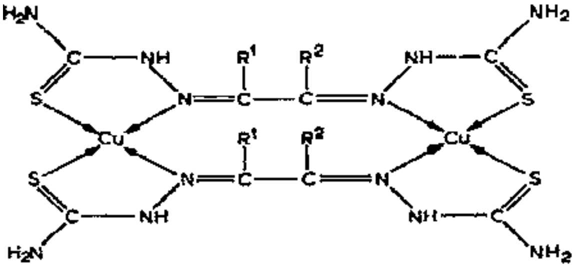


Fig. 13. Proposed structure dimer form of Cu(KTS).

the temperature to that of liquid helium. The parameters found are shown in Table 5. It will be noticed that for the cationic species $Cu(BUTSC)_2^{2+}$ the g values are higher and the hyperfine coupling constants are lower than in the uncharged species $Cu(BUTSC\text{-}H)_2$. Blumberg and Peisach attribute this to increased delocalisation in the chelate ring of the latter complex. A more likely explanation is that it is the result of differences in the extent of axial bonding. Because of the bigger positive charge on the metal ion in the cationic species there will be more axial bonding arising through interaction with the solvent for this complex. This would lead to the observed changes in the parameters.

(iii) Mössbauer spectra

The Mössbauer spectra of a number of TSC complexes of iron(II), of general formula $FeTSC_2X_2 \cdot nH_2O$, have been reported [43, 67]. The isomer shifts (I.S.) and quadrupole splittings (Q.S.) in mm sec^{-1} are shown in Table 6. The anhydrous sulphate, $FeTSC_2SO_4$, has the largest Q.S. yet found for any iron compound [43]. It is high spin ($\mu_{eff} = 5.49\ \mu_B$) and the iron is in a distorted octahedral environment with the donor atom set $O_2N_2S_2$ (see Section C above, Table 3). The most surprising feature of the Mössbauer spectrum is that it shows only one pair of reasonably sharp lines in spite of the fact that the crystal structure contains two chemically different iron(II)

TABLE 6

Mössbauer parameters of some thiosemicarbazide and thiosemicarbazone complexes of Fe(II) and Fe(III)

Complex	T (°K)	I.S. (mm sec^{-1}) ^{a}	Q.S. (mm sec^{-1})	Ref.
(i) Thiosemicarbazide complexes				
$FeTSC_2SO_4$	300	1.27 ± 0.04	4.65 ± 0.04	43
	77	1.34 ± 0.04	4.36 ± 0.04	
	4.2	1.32 ± 0.04	4.36 ± 0.04	
$FeTSC_2SO_4 \cdot \frac{1}{2}H_2O$	300	1.23 ± 0.04	4.33 ± 0.04	67
	196	1.28 ± 0.04	4.35 ± 0.04	
	77	1.36 ± 0.04	4.38 ± 0.04	
$FeTSC_2Cl_2 \cdot 2H_2O$	300	1.26 ± 0.04	3.79 ± 0.04	67
	196	1.28 ± 0.04	3.78 ± 0.04	
	77	1.35 ± 0.04	3.78 ± 0.04	
$FeTSC_2(NO_3)_2 \cdot 2H_2O$	300	1.21 ± 0.04	3.81 ± 0.04	67
	196	1.28 ± 0.04	3.90 ± 0.04	
	77	1.30 ± 0.04	3.78 ± 0.04	
$FeTSC_2(NCS)_2 \cdot \frac{1}{2}H_2O$	300	1.24 ± 0.04	3.18 ± 0.04	67
	196	1.31 ± 0.04	3.20 ± 0.04	
	77	1.37 ± 0.04	3.20 ± 0.04	

(continued)

TABLE 6 (continued)

(ii) Thiosemicarbazone complexes

$Fe(PVATSC\text{-}H)_2\cdot H_2O$	300	1.22 ± 0.04	2.63 ± 0.04	69
	80	1.29 ± 0.04	3.31 ± 0.04	
$Fe(MePVTSC\text{-}H)_2$	300	1.14 ± 0.04	2.70 ± 0.04	69
	80	1.26 ± 0.04	2.90 ± 0.04	
$Fe(DAOTSC)_2Cl_2$	300	0.48 ± 0.04	0.68 ± 0.04	69, 70
	80	0.51 ± 0.04	0.77 ± 0.04	
$Fe(DAOTSC\text{-}H)_2$	300	0.30 ± 0.04	2.02 ± 0.04	70
	78	0.37 ± 0.04	2.02 ± 0.04	
$Fe(DAOMeTSC\text{-}H)_2$	300	0.53 ± 0.04	0.88 ± 0.04	70
	78	0.58 ± 0.04	0.88 ± 0.04	
$NH_4[Fe(SALTSC\text{-}2H)_2]$	300	0.44 ± 0.04	2.81 ± 0.04	69
	80	0.52 ± 0.04	2.92 ± 0.04	
$NH_4[Fe(PVATSC\text{-}2H)_2]$	300	0.41 ± 0.04	3.18 ± 0.04	69
	80	0.50 ± 0.04	3.18 ± 0.04	
$Fe(SALTSC\text{-}H)Cl_2\cdot 2\frac{1}{2}H_2O$	300	0.61 ± 0.04	0.86 ± 0.04	69
	80	0.70 ± 0.04	0.90 ± 0.04	
$Fe(SALTSC\text{-}H)Br_2\cdot 2\frac{1}{2}H_2O$	300	—	—	69
	80	0.71 ± 0.04	1.00 ± 0.04	

Complex	Spin state	T (°K)	I.S. (mm sec^{-1})	Q.S. (mm sec^{-1})	Isomer %	Ref.
(iii) Thiosemicarbazone complexes with spin cross-over						
$PyH[Fe(SALTSC\text{-}2H)_2]\cdot H_2O$	$^6A_1$	300	0.65 ± 0.04	0.63 ± 0.04	100	71
		280	0.69 ± 0.04	0.62 ± 0.04	76*	
		273	0.54 ± 0.04	0.74 ± 0.04	21	
		195	0.74 ± 0.04	0.65 ± 0.04	17	
		80	—	—	0	
$PyH[Fe(SALTSC\text{-}2H)_2]\cdot H_2O$	$^2T_2$	300	—	—	0	
		280	0.54 ± 0.04	2.58 ± 0.04	19*	
		273	0.50 ± 0.04	2.80 ± 0.04	79	
		195	0.51 ± 0.04	2.80 ± 0.04	83	
		80	0.55 ± 0.04	2.84 ± 0.04	100	
$H[Fe(5Cl\text{-}SALTSC\text{-}2H)_2]$	$^6A_1$	300	0.68 ± 0.04	0.72 ± 0.04	100	71
		246	0.72 ± 0.04	0.72 ± 0.04	33	
		195	—	—	0	
	$^2T_2$	246	0.51 ± 0.04	2.74 ± 0.04	67	
		195	0.51 ± 0.04	2.80 ± 0.04	100	
		80	0.54 ± 0.04	2.81 ± 0.04	100	
$H[Fe(5Br\text{-}SALTSC\text{-}2H)_2]\cdot \frac{1}{2}H_2O$	$^6A_1$	300	0.70 ± 0.04	0.60 ± 0.04	100	71
		195	0.77 ± 0.04	0.69 ± 0.04	63	
		80	0.79 ± 0.04	0.72 ± 0.04	7	
$H[Fe(5Br\text{-}SALTSC\text{-}2H)_2]\cdot \frac{1}{2}H_2O$	$^2T_2$	300	—	—	0	71
		195	0.46 ± 0.04	2.90 ± 0.04	29	
		140	0.52 ± 0.04	2.86 ± 0.04	66	
		80	0.55 ± 0.04	2.93 ± 0.04	93	
$NH_4[Fe(SALTSC\text{-}2H)(PVATSC\text{-}2H)]\cdot 1\frac{1}{2}H_2O$	$^6A_1$	323	three peaks in spectrum		38	69
		300	0.58 ± 0.04	0.68 ± 0.04	38	
		80	0.78 ± 0.04	0.77 ± 0.04	23	
$NH_4[Fe(SALTSC\text{-}2H)(PVATSC\text{-}2H)]\cdot 1\frac{1}{2}H_2O$	$^2T_2$	323	0.41 ± 0.04	2.86 ± 0.04		
		300	0.41 ± 0.04	2.86 ± 0.04	62	
		80	0.51 ± 0.04	3.00 ± 0.04	77	

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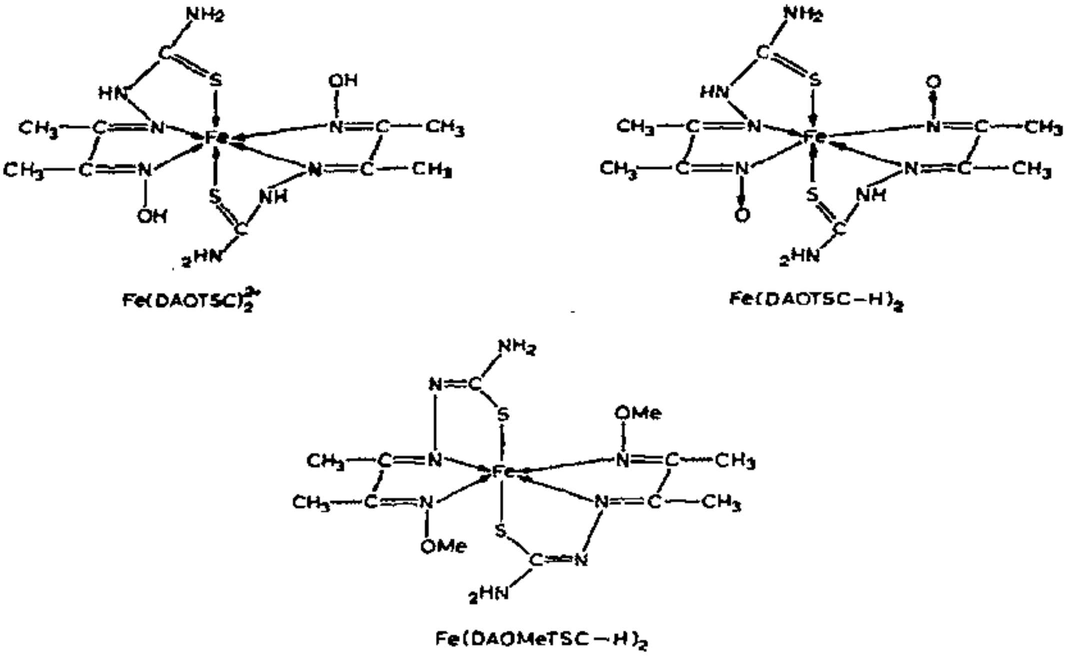
[a] I.S. values relative to sodium nitroprusside.

environments [28(b)]. Thus the two line spectrum must in reality consist of two two-line spectra perfectly superimposed. This implies that contrary to al expectation the net s electron density at the two iron nuclei must be identica in spite of the different geometries. It will be noticed from the data in Table that the sum of the Fe—O and Fe—N bond distances is almost the same for th *cis* and the *trans* unit with the *cis* having the shorter Fe—O distance and the *trans* having the shorter Fe—N distance. This may account for the identical I.S. values for the two units. It may also account for the identical Q.S. values since differences between the two isomer units as regards the valence and lattice contributions to the Q.S. may balance out.

The Q.S. value of $FeTSC_2SO_4$ was found to be relatively insensitive to temperature [43] showing that the ground state must be an orbital singlet well separated from other states. The sign of the electric field gradient was found to be positive [43] which is compatible, given the size of the Q.S., only with a d_{xy} or a $d_{x^2-y^2}$ ground state. A d_{xy} ground state is anticipated fc a tetragonally distorted octahedron. For the *trans* isomer there is quite clearl a compression along the N—Fe—N axis. The splitting of the one electron energy levels of a *cis* distorted octahedron does in fact give a $d_{x^2-y^2}$ ground state [57].

The I.S. values found by Ablov et al. for the chloride, nitrate and thiocyanate salts were essentially the same as that of the sulphate [67] but the Q.S. values found were appreciably smaller than that of the sulphate althoug they are still such as to rule out the possibility of a d_{xz} or d_{yz} ground state (see Table 6). Thus in the absence of any knowledge of the crystal structures of these compounds the best guess is that they have compressed tetragonal structures, although as we have seen in the case of the sulphate there is always some danger in assigning molecular geometries on the basis of spectral data alone. Ablov et al. [67] attempted to fit their Q.S. data using Ingalls' well known expression for high spin ferrous compounds [68]. This expresses the Q.S. value in terms of the rhombic splittings of the $^5T_{2g}$ ground term, Δ_1 and Δ_2, and of a single covalency parameter. It is significant that Ablov's attempt was unsuccessful. In the case of TSC complexes or similar compound it is clear that there will be considerable anisotropy in the covalency.

Ablov and co-workers have also used Mössbauer spectroscopy to study a number of thiosemicarbazone complexes of both iron(II) and iron(III). The inner complexes formed by the tridentate ligands, pyruvic acid thiosemicarbazone (PVATSC) and the thiosemicarbazone of methyl pyruvate (MePVTSC) [69], with iron(II) are high spin and have I.S. and Q.S. values in the usual range for high spin Fe(II). The donor atom set is $O_2N_2S_2$ for both compound The PVATSC complex has a quadrupole splitting which shows a more marke temperature dependence than that of the MePVTSC complex. This implies that the splittings Δ_1 and Δ_2 of the $^5T_{2g}$ ground term must be larger in the latter complex. However only for the former complex could the Q.S. data be fitted to Ingalls' expression [68]. Values of Δ_1 and Δ_2 of 260 and 520 cm^{-1} respectively were obtained. The fact that the authors were unable to fit the



$Fe(DAOTSC)_2^{2+}$ $Fe(DAOTSC-H)_2$

$Fe(DAOMeTSC-H)_2$

Fig. 14. Structures of $Fe(DAOTSC)_2^{2+}$, $Fe(DAOTSC—H)_2$ and $Fe(DAOMeTSC—H)_2$.

Q.S. data for PVATSC and other complexes they studied to Ingalls' expression does suggest that this expression is not valid in cases where there is appreciable covalency and bonding anisotropy.

With the thiosemicarbazone of diacetyl monoxime (DAOTSC) two types of complex can be formed with Fe(II), $Fe(DAOTSC)_2X_2$ and the inner complex $Fe(DAOTSC\text{-}H)_2$ (Fig. 14). The latter is formed by deprotonation of the OH group. Both types of complex are found to be diamagnetic and hence the quadrupole splittings arise because of differences in the covalency of the metal—ligand bonds and not because of anisotropy in the *d* electron distribution. The I.S. and Q.S. values found by Ablov et al. [69, 70] for the chloride and the inner complex are shown in Table 6. The lower I.S. value found for the inner complex can be attributed to an increase in 4*s* electron density resulting from the increased covalency of the monoxime nitrogen—metal bond. The authors consider that the major contribution to the e.f.g. comes from the three molecular orbitals to which the iron 4*p* orbitals contribute. In $Fe(DAOTSC)_2Cl_2$ if it is assumed that the two pairs of Fe—N bonds are equivalent then the e.f.g. results from the difference in covalency between these bonds and the Fe—S bonds. Ablov et al. assumed that the Fe—N bonds would be more covalent than the Fe—S bonds and hence that the sign of the e.f.g. would be negative [70]. In $Fe(DAOTSC\text{-}H)_2$ on the other hand the monoxime N—Fe bonds will be more covalent than the hydrazone N—Fe bonds and it was argued [70] that this leads to the much larger value of the Q.S. although the sign of the e.f.g. is still considered to be negative. In the inner complex

$Fe(DAOMeTSC\text{-}H)_2$ where DAOMeTSC is *O*-methyldiacetylthiosemicarbazone monoxime it is the thiol form of the ligand (Fig. 14) which has been deprotonated. Consequently the Fe—S bonds are more covalent than in the DAOTSC complexes and Ablov et al. predict a positive sign for the e.f.g. [70].

Ablov and co-workers have also studied the complexes formed with Fe(III) by salicylaldehyde thiosemicarbazone (SALTSC) which has the donor atom set $O_2N_2S_2$. The Mössbauer parameters for these compounds are shown in Table 6. The complexes $Fe(SALTSC\text{-}H)X_2 \cdot 2\frac{1}{2}H_2O$ where X = Cl, Br are high spin, but no indication is given [69] as to whether they are non-electrolytes or electrolytes and hence it is not clear what the coordination number is. The relatively large Q.S. value must arise from considerable asymmetry in the bonding as would be anticipated whatever the stereochemistry.

Interesting behaviour is observed for the complexes Cation$^+$ $Fe(SALTSC\text{-}2H)_2^-$. Thus the ammonium salt is low spin even at room temperature and has the expected large Q.S. value (see Table 6). This is essentially due to the asymmetry of the electron distribution in the t_{2g}^5 ground state configuration. However the corresponding pyridinium salt is completely in the high spin state at 300 K but must be close to the spin crossover point as by 280 K only 76% is in the high spin state and by 80 K it has passed completely into the low spin state. The difference in behaviour of the two salts may arise from different distortions of the basic $FeO_2N_2S_2$ octahedron depending on the different crystal packing requirements with different cations. It is however also possible that the same geometric isomer is not present in the two salts since both *cis* and *trans* isomers are possible. It is similarly found that $(NH_4)[Fe(PVATSC\text{-}2H)_2]$ is low spin at room temperature with only a small orbital contribution to the magnetic moment. This together with the fact that the Q.S. value shows no temperature variation between 300 and 80 K suggests that there must a considerable distortion. Surprisingly however the mixed complex $(NH_4)\text{-}[Fe(SALTSC\text{-}2H)(PVATSC\text{-}2H)] \cdot 1\frac{1}{2}H_2O$ is high spin at room temperature! It is however near the spin crossover point and there is already some of the low spin species present. Finally the complexes $H[Fe(5X\text{-}SALTSC\text{-}2H)_2]$ where 5X-SALTSC is either the 5-chloro- or the 5-bromo-derivative of SALTSC show similar behaviour to the pyridinium salt of $Fe(SALTSC\text{-}2H)_2^-$ being high spin at room temperature and low spin at 80 K.

E. INFRARED SPECTRA

(i) Ligand vibrations

An assignment of the major bands in the IR spectrum of TSC has been made by Mashima [72]. A re-examination of the spectrum of TSC as well as those of its salts, TSC.HX ($X = \frac{1}{2}SO_4, ClO_4, NO_3$, Cl, Br), and of acetone thiosemicarbazone (ATSC) by Campbell and Grzeskowiak [42] led to essentially the same assignments. Burns [73] made an assignment by comparison with thio-

TABLE 7

Infrared absorption frequencies (in cm^{-1})

Assignment	TSC	$CuTSC_2X_2$	$Cu(TSC)X_2$	$NiTSC_2SO_4 \cdot 3H_2O$	$Ni(TSC{\cdot}H)_2$	$NiTSC_3Cl_2$	$Ag(TSC)Cl$
ν(NH)	3360 s 3248 s 3170 s 3100 sh 2970 m	3320 s 3232 s 3070 s 2970 s 2900 sh	3395 s 3252 s 3180 s 3060 sh 2900 w	3350 s 3255 s 3180 m 3150 m 3125 m 3060 s 2955 s	3455 s 3285 m 3235 sh 3195 s 3185 sh 3120 sh 3095 s	3360 m 3260 s 3150 s	3340 m 3310 m 3250 s 3155 s
δ(NH_2)	1643 s 1617 s	1625 s 1602 s	1622 s 1606 s	1632 s 1603 s	1638 s 1597 s	1621 s 1600 s	1635 s 1612 s
δ(NH) + ν(CN)	1532 s 1508 sh	1562 m 1542 sh	1542 m 1530 sh	1563 w		1548 sh 1532 m	1540 m
ν(CN) + δ(NH)	1486 m	1440 s	1422 m	1434 m	1525 w		1480 m
Amide III	1315 m	1374 m	1388 m	1382 w 1340 w	1364 w 1323 w	1325 m	1292 m
Amide III	1284 m	1322 w	1303 w			1285 sh	1275 w
ρ(NH_2)	1220 w 1160 m	1195 m 1142 m	1192 s 1118 s	1237 m	1229 m 1139 w	1205 s 1117 m	1149 s
ω(NH_2)	1000 s	1000 w		990 w	1022 w		
ν(NN)					960 m		
ν(CS)	805 s	700 m	695 s	703 m	704 m 683 m	710 s	806 s 782 s

carbohydrazide for which he had made a normal coordinate analysis. His assignment of the bands in the region 1200—1500 cm^{-1} is somewhat different and he does not report the band at 1315 cm^{-1} found by other workers [42, 72, 74].

The spectra of the complexes $CuTSC_2X_2$ and $Cu(TSC)X_2$, for which the band frequencies are listed in Table 7, are quite characteristic for each type of complex and within the complex type there is very little change with change of anion. On complex formation most of the bands in the spectrum of TSC undergo frequency shifts and, in many cases, intensity changes. The most marked change is that of the 805 cm^{-1} band which is shifted almost 100 cm^{-1} to lower frequencies. This band is largely ν(CS) and a shift of this order would indicate a considerable change in the bond order, such as would result from the formation of a strong metal—sulphur bond. Similar shifts are observed in the spectra of $NiTSC_2SO_4 \cdot 3H_2O$ and $Ni(TSC\text{-}H)_2$ both of which contain *trans* square planar chromophores NiN_2S_2 (see Section C, Table 3). In both of these compounds the CS bond is appreciably longer than in TSC and the Ni—S bond length is relatively short. It would therefore seem reasonable to suppose that the situation is similar in the $CuTSC_2X_2$ complexes where the electronic spectra and far IR spectra suggest an essentially square planar environment for the Cu(II) ion [42, 75]*. The spectra of $NiTSC_2^{2+}$ and $CuTSC_2^{2+}$ are very similar except in the $\delta(NH_2)$ region so that it seems reasonable to assume that the geometry in the chelate rings is also similar. The spectra of $NiTSC_2^{2+}$ and $Ni(TSC\text{-}H)_2$ on the other hand show considerable differences as expected from the differences in the geometries of the chelate rings [26, 27] (Table 3). In the $Cu(TSC)X_2$ complexes on the other hand the electronic and far IR spectra indicate a 6-coordinate geometry about copper with TSC probably acting as a bridging ligand, and two types of Cu—X bond. This is certainly compatible with the very different spectra found for the $Cu(TSC)X_2$ complexes. However it is clear that the Cu—S bond strength must be much the same in both the 1:1 and the 1:2 complexes.

Burns reported that the 805 cm^{-1} band of TSC was only slightly shifted to 798 cm^{-1} in the spectrum of $NiTSC_3Cl_2$ [73], but Beecroft et al. found on the contrary that the band occurred at 710 cm^{-1} both in the spectrum of this compound and in that of the corresponding bromide [54]. There is the complication that we do not know if the $NiTSC_3^{2+}$ cation has the *fac* or *mer* configuration, although Jørgensen [81] believes that in the two tris complexes examined by him at least, the configuration is *mer*. In some ways it is surprizing that the ν(CS) band should occur at essentially the same frequency in the spectrum of $NiTSC_3Cl_2$ as in that of $NiTSC_2Cl_2$ since the Ni—S bond length in the tris cation is appreciably longer than in the diamagnetic square planar bis species (see Table 3). However unfortunately the more immediately relevant C—S bond length has not been reported for the tris cation. It is also

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* This has been confirmed for two of the complexes, $CuTSC_2SO_4$ and $CuTSC_2(NO_3)_2$, for which X-ray data exist [30, 31] (Table 3), although the former complex contains 5-coordinate copper with a *cis* arrangement of the TSC moieties.

worth noting that Haines and Sun reported [74] that the IR spectrum of *trans* $NiTSC_2(H_2O)_2^{2+}$ which is paramagnetic and has an Ni—S bond-length very similar to that of the tris species (see Table 3) is similar to that of the diamagnetic *trans* $NiTSC_2SO_4 \cdot 3H_2O$.

In the spectra of the *fac* and *mer* forms of Co(TSC-H)$_3$ and $CoTSC_3^{3+}$ the ν(CS) band appears about 100 cm^{-1} lower than in TSC itself [76]. In these complexes there is absolutely no doubt as to the high degree of covalency in the cobalt—sulphur bonds (see the discussion on the electronic spectra in Section F). In Ag(TSC)Cl the 805 cm^{-1} band is split but is not shifted much relative to TSC (see Table 7). Since the complex contains silver in two different environments the splitting is not unexpected but the small shift is rather surprizing in view of the usual class (b) behaviour of the Ag(I) ion.

The spectra of a number of nickel(II) thiosemicarbazone complexes containing 5-coordinate cations of approximately trigonal bipyramidal structure [35], NiL_2X^+ with X = Cl or Br, have been reported [54]. The ν(CS) band of the ligands is shifted by only ca. 40 cm^{-1} in the complexes. The C—S distance in one of the complexes, $NiTSCAC_2Cl_2 \cdot H_2O$, is essentially the same as that in $NiTSC_2SO_4$ but the Ni—S distance in the 5-coordinate species is much longer than in the square planar complex.

Gingras and co-workers have reported the IR spectra of a large number of thiosemicarbazones, both alkyl and aryl, *N*-substituted thiosemicarbazones and bis(thiosemicarbazones). In most cases they have prepared the copper(I) complexes of these compounds and they find that the ν(CS) band is a useful probe for complex formation since it either undergoes a shift to lower energies or disappears altogether [77]. A band in the region of 1100 cm^{-1} which in part involves CS stretching behaves in a similar way on complex formation. Similar behaviour has been observed for complexes of aryl thiosemicarbazones of Cu(II) [78], Pd(II) [79] and Co(II) [48]. In general where a shift is observed it is found that it is of the order 30—60 cm^{-1}. Complications can arise when absorption by the aldehyde or ketone part of the ligand occurs in the CS stretching region. In this case coupling will occur and assignment becomes difficult.

(ii) Metal—ligand vibrations

The far IR spectra of the complexes $CuTSC_2X_2$ (X = ½SO$_4$, NO$_3$, ClO$_4$, Cl, Br) and Cu(TSC)X$_2$ (X = Cl, Br) have been discussed [75]. Whilst these authors did find bands which they assigned as due mainly to copper—ligand stretching vibrations, they also concluded that in the absence of a full coordinate analysis it was not very meaningful to assign them as ν(CuN) and ν(CuS) as TSC is a non-rigid molecule having low frequency vibrations with which they can couple. This is in contrast with the behaviour of complexes of rigid ligands such as pyridine where the amount of coupling between purely ligand modes and metal—ligand modes is negligible [80]. A band at 240 cm^{-1} in the spectrum of $CuTSC_2SO_4$ which was assigned as ν(Cu—OSO$_3$), confirmed the mid

IR finding that the SO_4 is coordinated in monodentate manner*. The other 2:1 complexes are essentially square planar and there are no ν(Cu—X) vibrations as such although there are, in the halides, some localised lattice vibrations which are X-sensitive. In the complexes Cu(TSC)X_2 the copper atoms are 6-coordinate with both halogen and TSC coordinated. They are thought to be halogen bridged with TSC bridging two copper atoms in the $[Cu—X_2]_n$ chains. It is interesting to note that when semicarbazide ($NH_2CONHNH_2$) is substituted for TSC there is a decrease in the ν(Cu—L) frequencies in spite of the lower mass of semicarbazide. This parallels the lower stability constants found for the semicarbazide complexes (see Table 1, Section B).

Barz and Fritz also reported some far IR data [45] for complexes $M(TSC)_2X_2$ (M = Co, X = Cl; M = Ni, X = Cl, I; M = Cu, X = Cl, Br; M = Zn, X = Cl, Br) and also $NiTSC_3Cl_2$. They have assigned bands as ν(M—N) and ν(M—S) and furthermore they consider the Cu(II) and Ni(II) complexes to be 6-coordinate with ν(M—Cl) frequencies close to 300 cm^{-1}. This assignment seems almost certainly wrong as the $NiTSC_2X_2$ complexes are diamagnetic [46, 54, 73] and have electronic spectra typical of square planar species [54, 74]. Furthermore the electronic spectra are identical with those of the corresponding sulphate [54, 74] which is known to have a square planar structure (see Table 3, Section C). These authors also report some far IR data for some nickel, copper and zinc complexes of two thiosemicarbazones, ISTSC and MeISTSC. On the basis of mid IR data which they do not quote, they assert that the coordination behaviour of the ligands is as follows: (i) in Cu(I)L_2X and Zn(II)L_2X_2 coordination is through N^1 and N^3 of the TSC moiety; (ii) in M(II)L_2X_2 (M = Fe, Co, Ni) it is through N^3 and S of the TSC moiety that coordination occurs, as in TSC complexes; and (iii) in Cu(II)-(L—H)X and in 6-coordinate Ni$(L—H)_2$ the ligands are terdentate, bonding to the metal through O, N^3 and S. Only in the Cu(II) compounds is the halogen thought to be coordinated and the frequencies found are thought to be typical of terminal, i.e. not bridging, Cu—X bonds. The rather high frequency found for ν(Cu—Cl) in Cu(MeISTSC-H)Cl could well indicate a tetrahedral environment for the Cu(II) ion. The data are shown in Table 8. It is unfortunate that this paper [45] is incomplete both as regards data referred to but not quoted numerically and as regards any arguments to justify the assignments made.

The far IR spectral data for the complexes NiL_2X_2 (L = TSCAC, CPTSC and MeBUTSC; X = Cl, Br) have been reported [54]. The single Ni—X bond in the 5-coordinate, approximately trigonal bipyramidal chromophores, $NiN_2S_2X^+$ is in the equatorial plane in the one compound, $NiTSCAC_2Cl_2 \cdot H_2O$, for which the structure is known [35]. The ν(Ni—X) bands are of low intensity, in contrast with those found in tetrahedral species, and occur at frequencies which lie between those found for tetrahedral species and those found for 6-coordinate species. The ν(Ni—L) vibrations occur at very similar frequencies to those found for the square planar $NiTSC_2X_2$ complexes. This is somewhat

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* These spectroscopic findings were later confirmed by an X-ray structure determination [30].

TABLE 8

Characteristic frequencies in the far infrared spectra

Compound	ν(M—X)	ν(M—L)	ν(M—O)	δ(M—X)	Ref.
$Cu(TSC)Cl_2$	312 vs; 234 s	216 s		179 m	75
$Cu(TSC)Br_2$	251 s; 184 s	196 s		147 s	75
$CuTSC_2Cl_2$	160 m [a]	289 mw; 264 vs			75
	(266)	(288.5); (190)		(155)	45
$CuTSC_2Br_2$	105 m [a]	286 m; 240 vs			75
	(239)	(286); (185)		(130)	45
$CuTSC_2SO_4$		273 m; 260 vs	240 ms		75
$CuTSC_2(NO_3)_2$		285 mw; 230 vs			75
$CuTSC_2(ClO_4)_2$		286 mw; 220 vs			75
$CuISTSC_2Cl$		279		209	45
$CuISTSC_2Br$		276		179	45
Cu(ISTSC-H)Cl	313	283; 206	439		45
Cu(ISTSC-H)Br	264	297; 207	436		45
$CuMeISTSC_2Cl$		286			45
Cu(MeISTSC-H)Cl	335	283; 209	430		45
$NiTSC_2Cl_2$	174 s	286 s			54(a)
	(294)	(250); (201)		(167)	45
$NiTSC_2Br_2$	112 m	270 s			54(a)
$NiTSC_2I_2$	(245)	(250; 195)		(136)	45
$NiTSC_3Cl_2$		250; 230			45
$Ni(ISTSC\text{-}H)_2$		243; 221	436		45
$Ni(MeISTSC\text{-}H)_2$		244; 224	436		45
$NiTSCAC_2Cl_2 \cdot H_2O$	250 m	294 sh; 298 s			54(a)
$NiTSCAC_2Br_2 \cdot H_2O$	219 m	276 sh; 256 s			54(a)
$NiCPTSC_2Cl_2$	256 m	286 m; 240 m			54(a)
$NiCPTSC_2Br_2$	219 s	282 s; 230 m			54(a)
$NiMeBUTSC_2Cl_2$	242 s	292 s; 268 s			54(a)
$NiMeBUTSC_2Br_2$	198 s	280 s; 262 s			54(a)
$NiCPETSC_2Cl_2$	270 s	294 s; 242 m			54(b)
$NiCPETSC_2Br_2$	222 m	290 s; 242 s			54(b)
$NiCHTSC_2Cl_2$	264 s	292 m; 240 m			54(b)
$NiCHTSC_2Br_2$	224 m	280 s; 238 m			54(b)
$CoTSC_2Cl_2$		293; 279			45
$ZnTSC_2Cl_2$		256; 234			45
$ZnTSC_2Br_2$		266; 235			45
$ZnISTSC_2Cl_2$		252		155	45
$ZnISTSC_2Br_2$		229		139	45
$ZnMeISTSC_2Cl_2$		267			45

s strong; m medium; mw weak to medium; w weak; sh shoulder; all frequencies are in cm^{-1}.

[a] localised lattice vibrations.

surprising in view of the smaller shift observed for the ν(CS) vibration in the 5-coordinate species (see Section E (i)).

F. ELECTRONIC SPECTRA

The ligand field strength of sulphur has been found to vary more than that of any other donor atom, variations of up to 50% being known [81, 82]. This is probably due to the variation in π-bonding effects according to whether the sulphur has two or three lone pairs as in thioketones, $>C=S$, or mercaptide ions, $R-S^-$, which allows ample scope for M—S π-bonding, or only one lone pair as in SO_3^{2-} where it will be used for σ-bonding. Jørgensen has suggested that the position of a sulphur ligand in the spectrochemical series will depend on the difference between the amount of σ- and π-bonding involving S and their consequent anti-bonding effect on the metal *d* electrons [81].

Both the diffuse reflectance and absorption spectra of the complexes $CuTSC_2X_2$ ($X = \frac{1}{2}SO_4, ClO_4, NO_3$, Cl, Br) and $Cu(TSC)X_2$ (X = Cl, Br) have been studied [14, 42]. In aqueous solution all the complexes $CuTSC_2X_2$ have the same spectrum which has been shown to be that of $CuTSC_2aq^{2+}$ so that the effective chromophore is $CuO_2N_2S_2$ assuming two water molecules in the axial positions of a tetragonal cation. The overall band shape is typical for a tetragonal Cu(II) species with the maximum separated by about 2000 cm^{-1} from a fairly well defined shoulder on the low energy side. The maximum in the spectrum of the corresponding semicarbazide complex (effective chromophore CuO_4N_2) is displaced 2000 cm^{-1} to lower energies, so that TSC must lie above its oxygen analogue in the spectrochemical series. The relatively high extinction coefficients for the TSC complex (ϵ 176) is some evidence of appreciable covalency in the M—S bond, especially as, the probably symmetry being D_{2h}, the complex has a centre of symmetry (for the semicarbazide analogue the value of ϵ is only 36). The slightly lower value of ϵ found for the species $Cu(TSC)aq^{2+}$ (effective chromophore CuO_4NS) lends support to this view especially as it must have lower symmetry.

In the solid state all the complexes $CuTSC_2X_2$ except the sulphate have essentially the same spectrum with two fairly well resolved maxima at ca. 15000 and 19000 cm^{-1}, which is typical of a square planar Cu(II) chromophore presumably $CuTSC_2^{2+}$. The differences which do occur as X is varied can be attributed to crystal packing effects. The structure of $CuTSC_2SO_4$ is somewhat different [30] being square pyramidal with the TSC ligands in a *cis* configuration. However the visible spectrum is very similar to that of $CuTSC_2aq^{2+}$.

The spectrum of $CuTSC_2aq^{2+}$ also has a band at 28,200 cm^{-1} (ϵ 5817) with a shoulder on the high energy side at ca. 31,800 cm^{-1} (ϵ 3700) which must be due to charge transfer. Comparison with the spectrum of the analogous selenosemicarbazide species where the maxima are found to be shifted to lower energies, 29,000 cm^{-1} (ϵ 6000) and 24,400 cm^{-1} (ϵ 4300), confirm that this must be L→M transfer from sulphur to copper [14]. This is also confirmed by the shift to lower energies in less coordinating solvents such as ethanol [42]. Intense bands in the same region are also found in the solid state spectra.

The reflectance spectra of the $Cu(TSC)X_2$ species (X = Cl, Br) are typical of tetragonal Cu(II) compounds and a structure similar to that [83] of $Cu(1,2,4\text{-triazole})Cl_2$ involving $[CuX_2]_n$ chains with bridging TSC, has been proposed [42]. The solid complexes are not soluble in water but the *d—d* spectrum of the species $Cu(TSC)aq^{2+}$ has been obtained from solutions prepared from copper nitrate [14], the maximum being found about 1000 cm^{-1} lower than in the solid halide complexes. However in the aquo species TSC must be chelating not bridging. The sulphur—copper charge transfer band is found at 31,430 cm^{-1} (ϵ 3220) for the aqueous species and at 29,410 cm^{-1} (ϵ 2600) for $Cu(TSC)Cl_2$ dissolved in methanol [42]. The most interesting point is that whereas in the 2:1 complex there is a two band system in the 1:1 complex there is a single band.

TSC forms two series of complexes with nickel(II), low spin red complexes, $NiTSC_2X_2$ and high spin blue complexes, $NiTSC_3X_2$ [44]. The solution [73, 81] and solid state [54, 81] spectra of the 3:1 complexes show them to contain an essentially octahedral chromophore, $NiTSC_3^{2+}$, and only the $^3A_{2g} \rightarrow {}^3T_{2g}$ transition (in O_h symmetry) shows the marked splitting which might be anticipated with an NS donor set (it is not really possible to say whether the $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ transition is split because of an intense charge-transfer band which is adjacent to the one component which has been identified). Jørgensen [81] takes the former splitting as evidence for a *mer* configuration. From Burns' data [73] the value of B is calculated to be about 830 ± 30 cm^{-1} which is a reduction to about 80% of the free ion value of 1040 cm^{-1}. The lower value is the more likely as there may well be a second component of the $^3A_{2g} \rightarrow {}^3T_{1g}(P)$. transition masked by the charge-transfer band. The solid complexes $NiTSC_2X_2$ have spectra typical of square planar Ni(II) complexes, with one or two very weak bands due to spin-forbidden transitions near 10 kK and more intense spin-allowed bands at ca. 16, 19 and 23 kK [54, 73]. These energies are very similar to those found for other sulphur-containing ligands, e.g. nickel(II) thioglycollate [81] with bands at 16.4, 19.5 and 24 kK. $NiTSC_2SO_4$ contains both *cis* and *trans* $NiTSC_2^{2+}$ (Table 3, ref. 22) but its spectrum is not noticeably different from that of other red complexes $NiTSC_2X_2$. However the spectrum of *cis* $NiTSC_2(NO_3)_2$ does appear to be significantly different from those of the *trans* complexes [74].

Not all the red complexes are soluble in water but those which are dissolve to give blue solutions [44, 74], all of which have the same spectrum which is that of a tetragonal species. However Haines and Sun have pointed out that this spectrum differs appreciably from that of solid *trans*$[NiTSC_2(H_2O)_2]\cdot(NO_3)_2$ [74]. It is possible that in solution there is an equilibrium involving this species and $NiTSC_3^{2+}$ whose spectrum is quite similar, though not quite identical, to that of the blue solutions of $NiTSC_2X_2$.

The solid state spectra [74] of *cis* and *trans* $MTSC_2X_2$, where M = Pd(II), Pt(II), and those of the corresponding inner complexes $M(TSC\text{-}H)_2$ are typical of square planar complexes of these metal ions. Although the overlap of the *d*—*d* bands with the charge-transfer bands makes interpretation difficult there do appear to be some differences in the spectra of the *cis* and *trans* species. However the major differences between the solution spectra of *cis* and *trans* $PdTSC_2aq^{2+}$ are largely in the charge-transfer bands and in the internal ligand transitions (42.3 and 37.45 kK for the *trans*, 42.9 kK for the *cis* species).

In the presence of air Co(II) salts react with TSC to give complexes containing the cation $CoTSC_3^{3+}$ which has been shown to exist in two isomeric forms [76, 84], the *fac* and the *mer*. The corresponding forms of $Co(TSC\text{-}H)_3$ are also known [76, 84]. The relatively high extinction coefficients can be attributed in part to the lack of a centre of symmetry as the $^1A_{1g} \rightarrow {}^1T_{2g}$ transition (in O_h symmetry) is more intense in the lower symmetry *mer* isomer (maximum symmetry C_{2v}). However the high ϵ values are also probably due in part to the strongly covalent cobalt—sulphur bonds. Sun and Haines [76] resolved both the *cis* and *trans* isomers of $CoTSC_3^{3+}$ into their optically active forms using silver antimonyl tartrate, although they were unable to remove the resolving agent and had to make ORD and CD measurements on the diastereoisomers themselves (the resolving agent does not exhibit circular dichroism in the region of interest). They attributed the high intensity of the CD bands in the region of the $^1T_{1g}$ absorption to sulphur—cobalt π-bonding, pointing out that the CD band intensity was higher in the *fac* than in the *mer* isomer as might be expected, since in the *fac* isomer the sulphur donor atoms will not be competing for the same metal *d*-orbital. Using their data for the absorption bands the value of *B* is calculated to be ca. 300 cm^{-1} as compared with the value of 450 cm^{-1} found for the species $Co(en)_3^{3+}$. This result demonstrates clearly the covalency which has been introduced by the sulphur atom. The *fac*$(+)_{589}$ and *mer*$(+)_{589}$ $CoTSC_3^{3+}$ cations were assigned a Λ configuration while the *fac*$(-)_{589}$ and the *mer*$(-)_{589}$ isomers are thought to have a Δ configuration [76].

Jones and McCleverty recorded the spectra of a number of square planar bis(thiosemicarbazone) nickel(II) complexes but found them difficult to interpret [85]. The complexes formed with the bis(thiosemicarbazones) of glyoxal, pyruvaldehyde, biacetyl (these ligands are as in Fig. 13 with R_1 = H, H, Me and R_2 = H, Me, Me respectively) and cyclohexane-1,2-dione are green-brown and have absorptions at ca. 14,000 cm^{-1} ($\epsilon < 1000$), 22—24,000 cm^{-1} (usually resolved into two bands, $\epsilon \approx 15{,}000$) and ca. 30,000 cm^{-1} ($\epsilon \approx$ 7000). The complexes with the bis(thiosemicarbazones) of camphorquinone, hexane-2,5-dione, hexene-2,5-dione and phthalaldehyde on the other hand are red and have three or four absorption bands between ca. 15,000 cm^{-1} and 30,000 cm^{-1} (with widely varying extinction coefficients) as well as very intense bands above 33,000 cm^{-1} assigned as ligand π—π^* transitions. In both series of complexes the absorptions between ca. 14,000 and 20,000 cm^{-1} were assigned as *d*—*d* transitions whilst the bands between 20,000 and 30,000 cm^{-1} were assigned as charge transfer, probably *d*—π^*, by comparison with the spectral analyses of square planar chromophores of nickel(II) carried out by Bosnich [86].

The spectra of Cu(KTS) [62, 85] and of a number of closely related Cu(II) bis(thiosemicarbazone) complexes [87] (see Fig. 13) have two bands, often only partially resolved, at about 20,000 cm^{-1} ($\epsilon \approx 3500$—7000) and another pair of bands, again often only partially resolved, at about 30,000 cm^{-1} ($\epsilon \approx 7000$—$20{,}000$). Blumberg and Peisach [62] have proposed, by analogy with certain intensely absorbing copper proteins, that in spite of the high intensity, the 20,000 cm^{-1} bands are d—d transitions. Hatfield has carried out a semi-empirical molecular orbital treatment using the Wolfsberg—Helmholz approximation in order to try and fit the observed spectrum of diacetylbis(thiosemicarbazone) copper(II) (as Fig. 13 with $R_1 = R_2 = CH_3$) [66]. Taking the plane of the molecule as the xy plane the ground state ($^2B_2$ in C_{2v} symmetry) is an anti-bonding σ combination of copper d_{xy} and ligand σ-orbitals. The most important result of the calculation is that regardless of the input assumptions very large ligand orbital contributions to the ground state are found. The calculated d population lies between 0.287 and 0.445, depending on the input assumptions, while the value calculated from the expression [89]

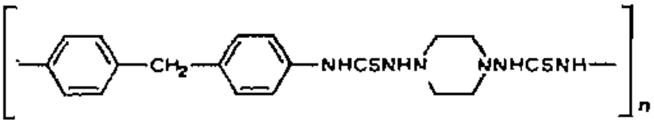
$$g_{\parallel} = 2.0023 - (8\lambda\Delta E_{xy-x^2-y^2})P_d^*$$

using the experimental value of $g_{\parallel}$ is 0.362. Using the experimental value of the ^{14}N ligand hyperfine splitting the value of the nitrogen MO coefficient in the ground state is calculated to be 0.565. The value calculated using the MO treatment lies between 0.548 and 0.357. The high observed extinction coefficients for the bands in the 20,000 cm^{-1} region are adequately explained by the large ligand orbital contributions to the ground state. Bähr was the first to report the preparation of copper(II) and nickel(II) bis(thiosemicarbazones) of the type shown in Fig. 13 and he was also the first to examine their electronic spectra albeit only over the range 13,333 to 25,000 cm^{-1} [88]. He found that the visible bands were relatively insensitive to change of solvent e.g. with $R_1 = CH_3$, $R_2 = n$-butyl the spectrum was much the same in benzene, ethanol and pyridine. Thus axial coordination by the solvent must be very weak. The complexes dissolve in concentrated sulphuric acid to give the "outer complexes", i.e. protonation of the ligand occurs, with a corresponding change of colour. The spectra of the "outer complexes" resemble that of $CuTSC_2SO_4$ or $CuTSC_2^{2+}$ with a maximum at 16—17,000 cm^{-1} and a shoulder at 14—15,000 cm^{-1}. The extinction coefficients are also much lower being in the region 500—1000 [90]. In the protonated form of the ligand the TSC skeleton is as in Fig. 1 rather than as in Fig. 5 with the result that the sulphur atom must be less polarisable. This would account for the decrease in the extinction coefficients. The shift to lower frequency is the result of the greater degree of axial coordination, itself the result of the larger positive charge on the copper(II) ion.

G. STRUCTURE AND STEREOCHEMISTRY

As we have seen TSC itself is normally a bidentate ligand which bonds to metal ions through the sulphur and hydrazinic nitrogen atoms. Neither of these donor atoms is sterically hindered so that it might be anticipated that the stereochemistry of TSC complexes would be similar to that of complexes formed with other bidentate ligands such as ethylenediamine. However the sulphur donor atom is very polarisable so that TSC not only exerts a strong ligand field but it is also responsible for the considerable reduction in the Racah electronic repulsion parameter *B* which is observed. Thus Ni(II) forms two series of complexes, low-spin square planar species $NiTSC_2X_2$ and high-spin octahedral species $NiTSC_3X_2$. Furthermore under alkaline conditions the ligand in its thiol form readily undergoes deprotonation (see Section C, Fig. 5). The anion $(TSC\text{-}H)^-$ contains the highly polarisable CS^- group. Copper(II) salts are reduced under these conditions to give Cu(TSC-H) and nickel(II) salts give only one complex $Ni(TSC\text{-}H)_2$ [1].

Jensen found [1] that N^1-substituted TSC's reacted with nickel(II) salts much as TSC itself giving two series of complexes NiL_2X_2 and NiL_3X_2. However N^1,N^2-disubstituted TSC's gave only square planar species. Although the use of substituted TSC's has been proposed for the analytical determination of some metals [91, 92] little or no structural information about such complexes has been reported in the literature. An extremely interesting example fo an N^1,N^3-disubstituted TSC is the polythiosemicarbazide formed by the reaction between *N,N'*-diaminopiperazine and methylenebis(4-phenyl isothiocyanate) which forms chelates with Ni(II), Co(II), Cu(II), Ag(I), Hg(II) and Pb(II) [93]. When the polymer is wet-spun into a DMSO solution of $CuCl_2$ a bronze-coloured fibre is obtained [93]. At p*H* 10 the formation of this copper chelate is accompanied by the liberation of the equivalent amount of hydrogen ion. Thus the ligand must be present as the deprotonated thiol form (see Section C, Fig. 5) and in the absence of intermolecular cross-linking the most likely structure would seem to be one with two TSC moieties coordinated to copper in a square planar arrangement similar to that shown in Fig. 13. This is undoubtedly a case where a copper(II) thiolato complex is stabilised relative to the copper(I) complex by a large entropy effect arising here because of the formation of three chelate rings. Similar behaviour obtains in the reactions of copper(II) salts with alkyl thiosemicarbazones. Thus monothiosemicarbazones, e.g. TSCAC, react with Cu(II) to give the Cu(I) complex while bisthiosemicarbazones, e.g. $KTSH_2$, give stable copper(II) complexes both in the neutral and in the deprotonated forms [90, 94]. Monothiosemicarbazones containing a third coordinating centre, e.g. PVATSC, are able to



form a second chelate ring and these too form stable copper(II) complexes [49].

Many aryl monothiosemicarbazones, both with [45] and without an extra coordinating centre [78], form stable copper(II) species and it must be presumed that this is so because of electronic effects arising from the electron withdrawing tendency of the aryl ring. This is particularly important in view of the suggestion by Leibermeister [9] that the successful anti-tubercular action of *p*-acetamidobenzaldehyde thiosemicarbazone (thiacetazone) involves formation of a copper(II) chelate of the ligand. Similarly O'Sullivan and Sadler [95] believe that isatin thiosemicarbazone and its derivatives owe their anti-viral action to chelation with metal ions among which copper(II) is the one most likely to form stable species.

Large numbers of copper(I) complexes of the thiolato type formed by both alkyl and aryl monothiosemicarbazones have been investigated by Gingras and co-workers [77]. Although no X-ray structure determination has ever been carried out for one of these complexes Gingras and Siriani have proposed [77d] that the properties of these compounds are compatible with polymeric structures involving linear coordination of the Cu(I) to sulphur and the hydrazinic nitrogen (N^3). For reasons which are not well understood N^1,N^1-dimethylbenzaldehyde thiosemicarbazone reacts with CuCl to give the copper(II) thiolato complex [77b].

The compound $NiTSCAC_2Cl_2 \cdot H_2O$ has been shown to consist of 5-coordinate trigonal bipyramidal cations $NiTSCAC_2Cl^+$, Cl^- and lattice water. The two S atoms are in the axial positions in the trigonal bipyramid [35]. Other nickel(II) halide thiosemicarbazone complexes appear, on the basis of electronic and vibrational spectra, to have similar structures [54]. The X-ray powder diagram of $CoTSCAC_2Cl_2 \cdot H_2O$ is identical with that of the nickel compound [96] and its electronic spectrum both in solution and in the solid state is very similar to that of known trigonal bipyramidal Co(II) chromophores [90]. It therefore seems probable that Co(II) halide thiosemicarbazone complexes will also have this structure. It might therefore appear that the trigonal bipyramidal structure is preferred to an octahedral or square planar one because of steric hindrance about the hydrazinic nitrogen atoms. However there are two pieces of evidence which suggest that the bulk of the sulphur atom must also be an important factor in determining the structure. Firstly the $NiTSCAC_2NO_3^+$ cation also has an essentially trigonal bipyramidal structure with a bidentate nitrate ion occupying a single coordination position [36]. Secondly the nickel(II) halide semicarbazone complexes have tetragonal structures [54a]. With aryl monothiosemicarbazones Ablov and Gerbeleu found [96] that only "inner complexes" ($Ni(L\text{-}H)_2$) were formed with Ni(II) salts in ethanolic solution. This is probably the result of electronic effects since in the neutral form of an aryl thiosemicarbazone the $-I$ effect of the aryl group would lower the polarisability of the hydrazinic nitrogen while in the thiolato form the polarisability of the sulphur would be much increased.

Ablov and Gerbeleu have also reported [96] that only 1:1 complexes

$ZnLX_2$ are formed when zinc halides react with simple alkyl thiosemicarbazones, e.g. TSCAC, even when an excess of ligand is used. Reaction of zinc halides with aryl monothiosemicarbazones under the same conditions produces only 1:2 complexes ZnL_2X_2. Zinc nitrate reacts with both types of ligand to give only 1:2 complexes $ZnL_2(NO_3)_2$. It is probable that the 1:1 complexes all have the tetrahedral structure found for ZnTSCAC Cl_2, but there is no experimental evidence available to indicate what structures the 1:2 complexes have. Tetrahedral cations ZnL_2^{2+}, 5-coordinate cations ZnL_2X^+ and octahedral species ZnL_2X_2 are all possibilities.

The only TSC complexes of iron known are the Fe(II) high spin tetragonal species $FeTSC_2X_2$ [43, 67]. However both high and low spin iron(II) and iron(III) complexes are formed with tridentate thiosemicarbazones [69—71]. Thus octahedral cationic species FeL_2^{2+} are high spin whereas "inner complexes" $Fe(L\text{-}H)_2$ are low spin. The octahedral Fe(III) species $Fe(L\text{-}2H)_2^-$ are either low spin or very close to the cross-over point. The compounds $Fe(SALTSC\text{-}H)X_2 \cdot 2\frac{1}{2}H_2O$ [69] are probably tetrahedral since they remain high spin over the temperature range 300—80 K. The structures of FeKTS. 2HCl and $Fe_2KTS_3 \cdot 2H_2O$ are unknown [94] but because of the steric constraints imposed by the organic ligand it seems likely that the former has a tetragonal structure with the Cl^- ions in the axial positions and a protonated form of the ligand coordinated in a square planar arrangement in the equatorial plane.

H. MONODENTATE BEHAVIOUR

In the vast majority of TSC and thiosemicarbazone complexes these ligands are bidentate and coordinate through both sulphur and the hydrazinic nitrogen. There are a few cases where monodentate behaviour is well established and where coordination is through sulphur only. Thus for Hg(II) the great similarity between the ΔG, ΔH and ΔS values for the formation of $HgTSC_2^{2+}$ and the corresponding values for the formation of $Hg(thiourea)_2^{2+}$ leaves little doubt that TSC is both monodentate and bound through sulphur (comparison with the data for the oxygen and selenium analogues of both ligands rules out the possibility that they are bound through nitrogen) [11]. Both the high affinity of mercury for sulphur and its preference for two linear bonds seem to be contributing factors. The Ag(I) ion is another well known class (b) acceptor with a marked affinity for sulphur. It is also well known that it rarely forms chelates. Thus it is no surprise to find that it forms complexes with TSC in which the latter is bound through sulphur only [22, 23] (Section C).

Samus and Ablov [97] have prepared the compound $CoCl(DMG)_2TSC$ (DMG = dimethylglyoximato) which is apparently a non-electrolyte. By analogy with the corresponding thiourea complex [98] they believe that TSC must be monodentate and bound through sulphur. However they do not present any real experimental evidence for this hypothesis so that although it is quite possibly correct on the assumption that Co(III) is 6-coordinate, it is also possible that it is wrong. Even if TSC is monodentate in this compound it may well be that it is bound through the hydrazinic nitrogen.

Thus to date the only substantiated cases of monodentate behaviour by TSC are in complexes of metal ions having a high affinity for sulphur with the consequence that in these complexes it is bound through sulphur only. No cases of monodentate behaviour with thiosemicarbazones have been reported.

I. CONCLUSIONS

In this review I have attempted to summarize the work on transition metal complexes of thiosemicarbazides and thiosemicarbazones which has relevance for our knowledge of the structure and bonding in these compounds. It is quite clear that the most important single factor affecting the behaviour of these ligands is the nature of the sulphur donor atom. Significantly there has been no report to date of such a complex in which the sulphur atom is not coordinated to the metal

The limited thermodynamic data show that the considerable stability of the complexes formed by these ligands with class (b) or marginally class (b) metal ions is due to a large enthalpy term which largely reflects strong metal—sulphur bonds. EPR, electronic and far IR spectra have also provided evidence for the existence of strong metal—sulphur bonds in these compounds. As well as being very polarisable the sulphur donor atom is also much larger than first row donor atoms. The size of the sulphur donor atom will exert a considerable influence on the stereochemistry of complexes formed by N^3 substituted TSC's and by thiosemicarbazones since in these ligands the hydrazinic nitrogen is sterically hindered.

There has been a great deal of work on the pharmacology of thiosemicarbazones and it has frequently been suggested that their activity is related to their ability to chelate trace metals. Most of the chemical research has concentrated on structure and bonding in these complexes in the solid state. Very little is known of their properties in solution and virtually nothing is known of their reactions. Clearly a great deal remains to be done before we can even start to rationalize the role of metal—thiosemicarbazone species in the pharmacological field.

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