

## Infrared Spectra of Thioamides and Selenoamides

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Through a study of the infrared absorption bands of about 150 thioamides, selenoamides, thioureas, and selenoureas (Tables 1-8) it has been possible to locate various characteristic bands. These are termed the thioamide A, B, . . . G bands — each of which behave in a characteristic way when the compounds are deuterated, *S*- or *Se*-alkylated, or transformed into metal complexes. Although it may be extremely difficult to decide from which molecular vibrations these bands originate, it is often easy to locate corresponding bands in the spectra of various thioamides. The A and E bands are only found in the spectra of primary thioamides, and the F band is not found in the spectra of tertiary thioamides. The remaining bands — B, C, D, and G bands — are found in the spectra of both primary, secondary, and tertiary thioamides. The G band seems often to be due to a fairly pure C—S (or C—Se) vibration although extensive coupling with N—H or other vibrations may occur. With a few exceptions, it is found below 800  $\text{cm}^{-1}$ , *i.e.* in a range usually cited for the single bond C—S stretching vibration. On substitution of sulfur with selenium this band is shifted 30–100  $\text{cm}^{-1}$  towards lower frequencies. Except for the G band the infrared spectra of corresponding thio- and selenoamides are so similar that it is concluded that there is no thioamide band which can rightly be classified as a “C=S band”.

New compounds prepared during this investigation are diseleno-malonamide, several thioureas, selenoureas, methiodides, and metal complexes of thioamides, selenoamides, thioureas, and selenoureas.

The infrared spectra of thioamides and related compounds have given rise to much discussion.<sup>1-10</sup> Most interest in this field has centered on the possibilities of making exact structural assignments rather than discussing the results from a practical point of view. Although the literature clearly indicates that useful diagnostic information can be obtained from the infrared spectra of thioamides, many new data has now been collected on frequency variations with the change of environment and it is the purpose of this report to present and analyze these findings. The present approach should be considered as an adjunct to the unequivocal interpretation of the bands, which involve theoretical calculations. Nevertheless, for identification purposes, the structural features are sufficiently clear to permit of considerable errors in the assignment

of bands to specific vibrations without invalidating the conclusions concerning the presence of the various thioamide structures.

We have been able to locate various characteristic bands in the spectra of thioamides, each of which behaves in a characteristic way, when the compounds are deuterated, *S*-alkylated, or transformed into metal complexes. Most of these bands undoubtedly arise from interactions between various vibrations so it would be arbitrary to use the concept of "a characteristic bond frequency". We have designated them in a non-committal way as A, B, . . . G bands. Several authors have spoken of the "Amide II band", "Amide III band" *etc.*, of thioamides but these terms are misleading because there is reason to believe (see later) that these bands will normally not correspond to the amide bands which have been designated by these terms.

In addition to the above-mentioned methods we have as already communicated in a preliminary note,<sup>11</sup> also used the replacement of sulfur by selenium as a diagnostic probe. The comparison of several spectra of thioamides, thioureas, and thiosemicarbazides with the spectra of the corresponding selenium analogues showed that the spectra of a sulfur compound and its selenium analogue were in most cases virtually superimposable down to 800–900  $\text{cm}^{-1}$ . This observation at once provides an answer to the much disputed question of the identification of the "C=S stretching vibration", the answer being that such a vibration is not present in the spectra of thioamides. The CS-vibration in the spectra of thioamides has predominantly single-bond character and so should be located in the 600–800  $\text{cm}^{-1}$  region.

Since the replacement of sulfur with selenium essentially changes only the bands due to CS vibrations, this method therefore almost works like an isotopic substitution. In the following we have briefly designated the substitution of sulfur with selenium "selenation" although this process, of course, cannot be carried out directly.

The substitution of sulfur with oxygen, on the other hand, changes the infrared spectrum so completely that it has not been possible to obtain much useful information from a comparison of the spectra of thioamides with the spectra of amides.

This paper is mainly concerned with infrared spectra of thioamides, thioureas, and their selenium analogues. Some data on the spectra of thiohydrazides and thiosemicarbazides (and their selenium analogues) will be included in the relevant places, but a more detailed discussion of the spectra of these compounds will be published in some forthcoming papers. Derivatives of thiocarbamic and dithiocarbamic acids also show some special features in their infrared spectra and will be treated in a future publication.

#### THE CHARACTERISTIC BANDS

*The A band.* The A band is a strong band, usually in the 1600–1650  $\text{cm}^{-1}$  region, found in the spectra of all thioamides, selenoamides, thioureas, and selenoureas, containing an unsubstituted  $\text{NH}_2$  group, *i.e.* the group  $-\text{CX}-\text{NH}_2$

(X = S or Se).<sup>\*</sup> Exceptionally, the band may be found at a little lower frequencies (dithiooxamide, 1582 cm<sup>-1</sup>; *N,N*-diphenylthiourea, 1595 cm<sup>-1</sup>) or higher frequencies (3-pyridinecarbothioamide, 1680 cm<sup>-1</sup>).

This band corresponds to the well-known "Amide II band of primary amides" (*cf.* Bellamy<sup>12</sup>) and has been shown (in many instances, by deuteration) to originate from the NH<sub>2</sub> deformation vibration. It was pointed out by Suzuki<sup>6,7</sup> that the NH<sub>2</sub> bending motion is necessarily coupled with the C—N stretching vibration of the neighbouring C—N bond. This is reflected, in our experiments, in the shift of the A band to higher frequencies on *S*- or *Se*-alkylation, salt formation, *e.g.* with hydrogen chloride (which is an *S*-protonation, *cf.* Janssen,<sup>13</sup> Kutzelnigg and Mecke<sup>28</sup>), or complex formation, by which the C—N bond assumes a higher degree of double bond character. One exception found was 3-pyridinecarbothioamide (thionicotinamide) which shows a shift of the A band on complex formation with CuCl to 1650 cm<sup>-1</sup>. The reason for this behaviour is that this thioamide is in equilibrium with its tautomeric thiol structure. Another exception is the complex formation of dithiomalonamide with cobalt(II) chloride. However, complexing of dithioamides may be a complicated reaction, *cf.* Hurd *et al.*<sup>14</sup>

The position of the A band can be used to distinguish these compounds from hydrazides and thiohydrazides. In these compounds, the NH<sub>2</sub> group is not adjacent to a CO or CS group and the NH<sub>2</sub> band will, therefore, be found at lower frequencies. In the spectra of 2-substituted thiosemicarbazides, H<sub>2</sub>N—CS—NR—NH<sub>2</sub>, two NH<sub>2</sub> bands are observed of which the one with the higher frequency must be ascribed to the thioamide NH<sub>2</sub> group.

Indirect evidence to support the above assignments is indicated by the absence of the A band in the spectra of all the compounds studied which have no free NH<sub>2</sub> group.

*The B band.* The B band is a strong band in the 1400—1600 cm<sup>-1</sup> range and appears in the spectra of all thioamides, thioureas, thiohydrazides, thiosemicarbazides, and their selenium analogues investigated in this laboratory.

This is a very characteristic band, usually very strong and somewhat broad, which is useful for distinguishing it from absorption peaks due, for example, to the phenyl group, which are generally sharp in shape. Furthermore, this band is very sensitive to complex formation and *S*-alkylation, and we have on no occasions been in doubt as to its location. It has been asserted that this band is missing in the spectra of primary thioamides, but this is actually not the case; however, it may be found at as low frequencies as 1400 cm<sup>-1</sup>, *e.g.* in the spectrum of thiobenzamide. Generally it is found between 1500 and 1600 cm<sup>-1</sup>.

In view of the major shift to higher frequencies observed by *S*-alkylation, a decisive feature of the B band must be a C—N vibration, the shift thus being

<sup>\*</sup> In spectroscopic literature, amides with the groups —CONH<sub>2</sub>, —CONHR, and —CONR<sub>2</sub> (R = alkyl or aryl) are usually distinguished by the terms primary, secondary, and tertiary amides. The same terms are, however, also used for mono-, di-, and triacylamines, and the *IUPAC Commission on the Nomenclature of Organic Chemistry*, therefore, does not recommend their use. Nevertheless, after some hesitation, we have decided to retain these terms because it is obviously more convenient to talk about primary, secondary, and tertiary thioamides than of "N-unsubstituted" "N-monoalkyl or N-monoaryl" and "N,N-dialkyl, N,N-alkyl-aryl or N,N-diaryl" thioamides.

explained by the increased double-bond character of the C—N bond following alkylation of the sulfur (or selenium) atom. However, a full explanation of this band must obviously be founded on the concept of mixed vibrations, the extent and type of which seem to be highly dependent on the environment of the C—N bond.

In the case of primary aliphatic thio- and selenoamides, extensive coupling seems to occur with CH, CH<sub>2</sub> or CH<sub>3</sub> vibrations.<sup>6,7</sup> The shift of the band in the spectrum of thioacetamide from 1470 cm<sup>-1</sup> to 1573 cm<sup>-1</sup> on *S*-methylation should probably be explained by an increased coupling of the CN and CH<sub>3</sub> vibrations rather than by an increased double-bond character of the CN bond. In secondary aliphatic thio- and selenoamides,<sup>8,15</sup> the frequency of the CN vibration is sufficiently near to that of the NH vibration for a coupling to occur. Accordingly, deuteration influences the B band of secondary thio- and selenoamides. Similar behaviour has been noted by Elmore<sup>3</sup> in the infrared spectra of cyclic secondary thioamides. We agree with this author in the assignment of the B band in tertiary thio- (and seleno-) ureas to the C—N grouping primarily; however, coupling with neighbouring alkyl groups cannot be excluded.

In the spectra of primary aromatic thioamides, the shift of the B band to slightly higher frequencies on deuteration cannot be explained by assuming coupling with the vibrations from the aromatic nucleus, as these are unaffected by deuteration. We therefore conclude that, in the B bands of these compounds, some admixture of the NH<sub>2</sub> band is present. The small shift, observed when going from thiobenzamide to selenobenzamide, also reveals a minor coupling with the C—S vibration. As expected, the B band in *N*-methylthiobenzamide is due to mixed C—N and N—H vibrations, as found in the aliphatic series.

We consider the B bands in the spectra of thio- and selenoureas to originate chiefly from the antisymmetric N—C—N stretching motion, though probably with some coupling with the CS (or CSe) and the NH and NH<sub>2</sub> vibrational modes, as is evident from deuteration and selenation experiments. That a coupling with the NH vibration has occurred in the spectra of secondary thioureas is also supported by the observation that the B bands occur as doublets in the spectra of thioureas of the type RNH—CS—NHR', unless the radicals R and R' are very similar in mass and structure (such as phenyl and *p*-tolyl), but not in the spectra of trialkylthioureas.

The B band resembles both the strong band near 1550 cm<sup>-1</sup> occurring in the spectra of cyclic compounds containing the —CS—NH— group (which was called the "thioureide band" by Randall *et al.*<sup>16</sup> (*cf.* also Refs. 3, 9, 38), and a strong band in the same region in the spectra of *N,N*-dialkyldithiocarbamates studied by Chatt, Duncanson and Venanzi.<sup>17</sup> The latter workers assign this band to the C—N stretching mode shortened under the influence of the

resonance structure  $R_2\overset{\oplus}{N} = C \begin{matrix} \diagup S^{\ominus} \\ \diagdown S^{\ominus} \end{matrix}$ . As discussed above, this is considered to

be an essentially correct description of the origin of the B band.

Other authors, on the other hand, have compared this band with the "amide II band of secondary amides", which is also a strong band near 1550 cm<sup>-1</sup>.

In our opinion, however, this comparison is misleading. Although the "amide II band of secondary amides" has some C—N character (*cf.* Miyazawa *et al.*<sup>18</sup>) a major component of this band is the N—H vibration. It, therefore, disappears on deuteration and is missing in the spectra of tertiary amides whereas the B band is influenced only little by deuteration and is strong also in the spectra of tertiary thioamides. Further, the B band also occurs in the spectra of primary thioamides whereas primary amides have only the "amide II band of primary amides" which corresponds to our A band. If at all, the B band is comparable with the "Amide I band" and not with the "Amide II band". Both the B band and the amide I band have their origin in the antisymmetrical vibration of the grouping N—C=X (X = O, S, Se), the main difference being that the stretching of the N—C=O grouping has predominantly C=O character whereas the stretching of the thioamide or selenoamide group has predominantly C=N character. In accordance herewith, it is the amide I band and not the amide II band which resembles the B band by being influenced by *O*-alkylation (formation of imido esters and isoureas), *O*-protonation<sup>13</sup> and complex formation.<sup>19</sup>

*The C band.* The C band is in most cases readily observed as a medium to strong band in the 1200–1400 cm<sup>-1</sup> region, although it may be found at slightly higher frequencies (*e.g.* thiourea, 1415 cm<sup>-1</sup>). We have found this band in the spectra of all thioureas and thioamides and their selenium analogues, and in the spectra of most thiohydrazides. However, the band is usually less pronounced for thioamides and thiohydrazides.

Like the B band, the C band is essentially composite in nature. It has been assigned to C—C vibration or to a mixture of NH<sub>2</sub> rocking and N—C—N and C—S stretching vibration.<sup>4</sup> Since, however, this band occurs also in the spectra of tertiary thioamides the NH<sub>2</sub> rocking mode cannot contribute substantially to this band. Furthermore, very little mixing with a CS vibration can occur since the C band is found in almost the same place in the infrared spectra of thio- and selenoureas.

The C band in thioureas and selenoureas is considered to be mainly due to the N—C—N grouping, in agreement with Rao *et al.*<sup>10</sup> However, in primary and secondary thioamides and thioureas, mixing occurs to a small degree with NH vibrations, as is apparent from deuteration studies. Nevertheless, this band is much less sensitive to deuteration than the amide III band of secondary amides and therefore they probably are not comparable.

Only a small shift of the C band of thioureas and tertiary thioamides is observed on *S*-methylation. No shift was observed on *S*-methylation of thio-benzamide, whereas the frequency of the C band of selenobenzamide was raised slightly on *Se*-methylation. In contrast, the C band of primary and secondary aliphatic thioamides is shifted significantly to higher frequencies on *S*-methylation. This difference can probably be attributed to the greater weight of the dipolar structure  $\text{H}_2\overset{+}{\text{N}}=\text{C}-\overset{-}{\text{S}}$  for thioureas and aromatic thioamides than for aliphatic thioamides, as is plausible from their dipole moments. The increase in polarity on *S*-alkylation will, therefore, be relatively greater for the aliphatic thioamides.

In aliphatic thioamides, coupling with CH, CH<sub>2</sub>, and CH<sub>3</sub> vibrations further seems to be of importance.<sup>6,7</sup>

*The D band.* A band of medium strength can be found in the 1000–1200 cm<sup>-1</sup> range in the spectra of most thioamides, thioureas, and their selenium analogues, with the exception of symmetrically aromatic disubstituted thioureas. Collard-Charon and Renon<sup>15,20</sup> considered this band to be due to the CS group; however, the changes induced on selenation seem to be much too small to justify this assignment. Further, our deuteration studies have shown it to be due chiefly to NH vibrations in secondary thioamides and most thioureas. Only in a few compounds, *e.g.* thioacetamide and thiourea, does the CS character seem to be recognizable, as the D band of such compounds is shifted to lower frequencies on *S*-alkylation, *i.e.* opposite to the B and C bands, reflecting the diminished double-bond character of the CS bond following the *S*-alkylation. However, even in these cases, the shifts are very small compared with those found for the B and C bands.

For other compounds a shift, equally small, to higher frequencies is observed on *S*-alkylation, which shows that the D band also has some C–N character. These observations indicate that a major contribution to the D band might be the symmetrical stretching vibration of the N–C–S grouping. *S*-Alkylation will affect the C–N and the C–S bond in an opposite way and the net result may therefore be small. However, as mentioned earlier, extensive coupling with N–H vibrations occurs in compounds with a primary or secondary thioamide group.

*The E band.* A characteristic band, usually in the range 800–900 cm<sup>-1</sup>, appears in the spectra of most thioureas and selenoureas with a primary amino group (except unsubstituted thiourea and selenourea) and thiosemicarbazides. It is also found in the spectra of some primary thioamides but is absent in others. The main contribution to this band is considered to be an NH<sub>2</sub> bending mode (wagging). This vibration may couple strongly with other vibrations which accounts for the absence of this band in the spectra of many primary thioamides. On *S*-methylation or complex formation it is often weakened and may disappear completely, probably because the wagging of the NH<sub>2</sub> group is more or less inhibited when the double-bond character of the C–N bond is increased.

The E band may be shifted significantly on selenation (see Table 5). However, the fact that it is very sensitive to deuteration and is not shifted, but only weakened, on *S*- or *Se*-methylation or complex formation, shows that it has its origin in NH<sub>2</sub> vibrations.

All spectra of thiosemicarbazides with an unsubstituted 1-NH<sub>2</sub> group further have a strong band near 1000 cm<sup>-1</sup> which may also be assigned to an NH<sub>2</sub> bending mode. In contrast to the 800 cm<sup>-1</sup> band, it is unaffected by *S*-methylation or complex formation but disappears on deuteration. It will be discussed more fully in a forthcoming paper on the infrared spectra of thiosemicarbazides.

*The F band.* A band near 700 cm<sup>-1</sup> seems typical for the spectra of most thioamides and thioureas. It has been assigned to C–N stretching or to a mixture of C=S and N–C–N stretching.<sup>4</sup> However, this band is common for thio- and seleno-compounds, is sensitive to deuteration, and is found in

the spectra of all thioamides and substituted thioureas except *N,N*-dialkylthioamides and tetraalkylthioureas. The main contribution to this band must therefore come from N—H vibrations.

*The G band.* The G band is the only band which shows a significantly different location for thio- and seleno-compounds. It is, therefore, associated with the  $\nu(\text{CS})$  or  $\nu(\text{CSe})$  vibration, and this is also substantiated by a shift of this band towards lower frequencies on *S*- or *Se*-alkylation or formation of metal complexes, reactions which diminish the double-bond character of the CS or CSe bond. The G band of primary and secondary thioamides and thioureas is slightly sensitive to *N*-deuteration which indicates some coupling with NH vibrations, and coupling may also occur with other vibrations.<sup>6,7</sup> On the whole, however, the G band is probably due to a fairly pure CS or CSe vibration. In the spectra of the thio compounds it is found in the range usually cited for the single-bond C—S stretching vibration (600—800  $\text{cm}^{-1}$ ) or in a few cases (thioformamides, dithioamides, tertiary thioamides) somewhat higher; for the seleno compounds it is found at 30 to 100  $\text{cm}^{-1}$  lower frequencies.

Earlier assignments for the CS stretching frequency have ranged as high as 1413  $\text{cm}^{-1}$  in thiourea,<sup>21</sup> 1130—1330  $\text{cm}^{-1}$  in substituted thioureas,<sup>22</sup> near 1100  $\text{cm}^{-1}$  in thiolactams,<sup>1</sup> 1360  $\text{cm}^{-1}$  in thiosemicarbazides,<sup>23</sup> 1000  $\text{cm}^{-1}$  in thiobenzanilide,<sup>2</sup> and 1216 or 980  $\text{cm}^{-1}$  in thioacetamide.<sup>5,24</sup>

It now seems fully substantiated that the CS band of thioamides and thioureas will normally be found below 800  $\text{cm}^{-1}$ .

#### DISCUSSION OF THE INFRARED SPECTRA OF INDIVIDUAL THIOAMIDES

*Thioformamides.* A detailed study of the infrared spectrum of thioformamide was first published by Davies and Jones.<sup>25</sup> More recently, Suzuki<sup>6</sup> supplemented this work with observations on *N,N*-dideuteriothioformamide and supported the assignments with theoretical calculations.

Both Davies and Jones and Suzuki agree in assigning the most intense band at 1433  $\text{cm}^{-1}$  chiefly to the  $\nu(\text{CN})$  vibration, but according to the calculations by Suzuki this vibrational mode couples almost completely with the  $\delta(\text{CH})$  vibration. The CN character of this B band is demonstrated by a major shift to 1610  $\text{cm}^{-1}$  in *S*-methylthioformamidium iodide. At the same time the A band, which must be due essentially to  $\text{NH}_2$  deformation as it is replaced by deuteration, shows an upward frequency shift from 1612 to 1680  $\text{cm}^{-1}$ , which also indicates that this band has some CN character. The B band is shifted slightly toward higher frequencies on deuteration.

The increase in frequency of the C band from 1324  $\text{cm}^{-1}$  to 1395  $\text{cm}^{-1}$  on *S*-methylation is consistent with the findings of Suzuki, who attributes it to a mixed CN and CH vibration. Davies and Jones assigned this band to the  $\delta(\text{CH})$  vibration and a band at 1288  $\text{cm}^{-1}$  to the NCS group, but these assignments should be reversed since the 1288  $\text{cm}^{-1}$  band is only little influenced by *S*-methylation.

According to Suzuki a band at 1125  $\text{cm}^{-1}$  should be due to an  $\text{NH}_2$  vibration with a small contribution from the CS vibration, but the band is unchanged on *S*-methylation. Instead, the D band is considered to be a band near 1000

Table 1. Infrared absorption bands ( $\text{cm}^{-1}$ ) of aliphatic thio- and selenoamides.

Compound	A	B	C	D	F	G
<i>Thioformamide and derivatives.</i>						
$\text{HCSNH}_2^*$	1615m	1433s	1324m	1006m	641m	830m
$[\text{HC}(\text{SMe})\text{NH}_2]\text{I}$	1680m	1610m	1395s	1015w	690w	791s
$\text{HCSNHMe}^*$	—	1550vs	1308s	992s	739m	874s
$[\text{HC}(\text{SMe})\text{NHMe}]\text{I}$	—	1601vs	1305m	{ 966m 991m	762m	824m
$\text{HCSNMe}_2$	—	1530vs	1401s	1130s	—	975s
$[\text{HC}(\text{SMe})\text{NMe}_2]\text{I}$	—	1645vs	1410m	1160m	—	860m
$\text{HCSNP}_3$	—	1500vs	1225s,br	1140s	—	{ 950s 965s
$[\text{HC}(\text{SMe})\text{NP}_3]\text{I}$	—	1615vs	1250vw	1160vw	—	—
$\text{HCSNP}_3$	—	1490vs	1299vs	1185m	—	944m
$[(\text{HCSNP}_3)_3\text{PtCl}_4]$	—	1530vs	1305s	1180w	—	{ 900m 910m
$[\text{HC}(\text{SMe})\text{NP}_3]\text{I}$	—	1582vs	1330w	1177w	—	885w
$\text{HCSenPr}_3$	—	1490vs	1295vs	1182m	—	816m
$[\text{HC}(\text{SeMe})\text{NP}_3]\text{I}$	—	1580vs	1305m	1192w	—	778m
$\text{HCSNHPh}$	—	1565s	1361s	975s	—	766s,sh
$[\text{HC}(\text{SMe})\text{NHPh}]\text{I}$	—	1680m	1410m	975vw	—	—
<i>Thioacetamide and derivatives.</i>						
$\text{CH}_3\text{CSNH}_2^*$	1648s	1482s	1393s	1305s	706s	718s
$[\text{CH}_3\text{C}(\text{SMe})\text{NH}_2]\text{I}$	1676s	1573s	1532m	1292s	804m	674m
$[\text{CH}_3\text{C}(\text{SCH}_2\text{COOH})\text{NH}_2]\text{Br}$	1690s	1600s	1555m	1290s	825s	680m
$(\text{CH}_3\text{CSNH}_2)_2\text{CuCl}_2^{\text{a}}$	1669m	1515m	1409w	1318s	769s	690m
$[\text{CH}_3\text{C}(\text{SH})\text{NH}_2]_2[\text{SnCl}_4]^{\text{a}}$	1669m	1548m	1416w	1312s	800s	676m
$\text{CH}_3\text{CSeNH}_2$	1650s	1482s	1410s	1290s	716m	615s
$\text{CH}_3\text{CSNHMe}^*$	—	1566s	1357vs	{ 1100s 956s	741m	680s



Table 1. Continued.

Compound	A	B	C	D	F	G
$[\text{CH}_3\text{C}(\text{SMe})\text{N}(\text{HMe})\text{I}]$	—	1625vs	1392m	{ 1100m 955m	735w	635m
$\text{CH}_3\text{CSeNHMe}$ 15	—	1565s	1365s	{ 1083s 936s	not investigated	
$\text{CH}_3\text{CSNMe}$	—	1530s	1388m	1010s	—	863m
$[\text{CH}_3\text{C}(\text{SMe})\text{NMe}_2]\text{I}$	—	1600vs	1402m	1005w	—	840w
$\text{CH}_3\text{CSeNMe}_2$	—	1539s	1389m	1009m	—	834m
$[\text{CH}_3\text{C}(\text{SeMe})\text{NMe}_2]\text{I}$	—	1600s	1400m	995w	—	820vw
$\text{CH}_3\text{CSNHPh}$	—	1525s	1370vs	1146s	—	709s
$[\text{CH}_3\text{C}(\text{SMe})\text{N}(\text{HPh})\text{I}]$	—	1571s	1405s	1169s	—	654s
$\text{NC-CH}_2\text{CSNH}_2$	1623vs	1460vs	1285m	1260s, br	695s	750m
<i>Higher thioamides.</i>						
$\text{CH}_3(\text{CH}_2)_6\text{CSNH}_2^*$	1640s	1440s	1420sh	1305m	716s	725m, sh
$[\text{CH}_2(\text{CH}_2)_6\text{C}(\text{SCH}_2\text{COOH})\text{NH}_2]\text{Br}$	1625m	1590w	1525m	—	722w	697m
$\text{CH}_3(\text{CH}_2)_4\text{CSNH}_2$	1635s	1440s	1405m	1300w	718s	725m, sh
$[\text{CH}_2(\text{CH}_2)_4\text{C}(\text{SCH}_2\text{COOH})\text{NH}_2]\text{Br}$	1630m	1590w	1535m	—	718w	697w
$\text{CH}_3\text{CH}_2\text{CSNHMe}^*$	—	1526s	1368s	1000s	670m, br	
$[\text{CH}_3\text{CH}_2\text{C}(\text{SMe})\text{N}(\text{HMe})\text{I}]^*$	—	1620vs	1400m	990m	721m	664m
$\text{CH}_3(\text{CH}_2)_2\text{CSNHMe}^*$	—	1520s	1372s	1012s	700m, br	
$[\text{CH}_3(\text{CH}_2)_2\text{C}(\text{SMe})\text{N}(\text{HMe})\text{I}]^*$	—	1620vs	1400m	1002m	720w	692w
$[\text{CH}_2\text{CH}(\text{CH}_2)_2\text{CSNHPh}]^*$	—	1499s	1400vs	1011vs	690m, br	
$[(\text{CH}_2)_2\text{CHC}(\text{SMe})\text{N}(\text{HPh})\text{I}]^*$	—	1600vs	1460m	1000m	727m	673m
$\text{CH}_3(\text{CH}_2)_3\text{CSNHMe}^*$	—	1520s	1372s	1024s	733s	700s, br
$[\text{CH}_3(\text{CH}_2)_3\text{C}(\text{SMe})\text{N}(\text{HMe})\text{I}]$	—	1620vs	1398m	{ 989m 1010m	732m	698w

\* The compounds marked with an asterisk were investigated by deuteration.

$\text{cm}^{-1}$ . It was assigned to a CH vibration by the above-mentioned authors, but it almost disappears on addition of methyl iodide to thioformamide, whilst the frequency remains essentially unchanged ( $1013 \text{ cm}^{-1}$ ), so at least some skeletal vibrational influence must occur.

The band at  $641 \text{ cm}^{-1}$  is shifted on *S*-methylation to  $690 \text{ cm}^{-1}$  and disappears on deuteration; it can thus safely be identified with the F band due to the  $\text{NH}_2$  group. The G band is found at  $830 \text{ cm}^{-1}$  and is shifted to  $791 \text{ cm}^{-1}$  on *S*-methylation. An investigation of selenoformamide would definitely decide whether this band arises from the CS vibration, but attempts to prepare this hitherto unknown compound were unsuccessful.

The infrared spectra of *N*-methyl- and *N,N*-dimethylthioformamide have, of course, no A bands, but they show strong B bands at  $1550 \text{ cm}^{-1}$  and  $1530 \text{ cm}^{-1}$ , respectively. Both bands are shifted to higher frequencies on *S*-methylation, characterising them as due essentially to the CN grouping. However, according to Suzuki, this vibration in the monomethyl derivative couples with NH and  $\text{CH}_3$  vibrations.

Only very small changes occur in the  $1100\text{--}1500 \text{ cm}^{-1}$  range on *S*-methylation of *N*-methylthioformamide; therefore the presence of the C band could not be shown in this way, but was assigned according to Suzuki.<sup>8</sup> However, the  $992 \text{ cm}^{-1}$  band is notably weakened and must, therefore, be the D band. This is in agreement with Suzuki, who attributes this band to CN and CS vibrations. On *S*-methylation, the F band is easily recognized by a shift from  $739 \text{ cm}^{-1}$  to  $762 \text{ cm}^{-1}$ , and the G band by a shift in the opposite direction from  $874 \text{ cm}^{-1}$  to  $824 \text{ cm}^{-1}$ .

The C and D bands of *N,N*-dimethylthioformamide are apparent by the shifts of the bands at  $1401 \text{ cm}^{-1}$  and  $1130 \text{ cm}^{-1}$  to  $1410 \text{ cm}^{-1}$  and  $1160 \text{ cm}^{-1}$ , respectively, on *S*-methylation. No F band is present, the  $\text{NH}_2$  group being fully substituted. The G band is considered to be a strong band at  $975 \text{ cm}^{-1}$ , shifted to  $860 \text{ cm}^{-1}$  on *S*-methylation. This is an unusual high frequency for a G band, but this assignment is confirmed by consideration of the spectra of other *N,N*-dialkylthioformamides and especially by comparison of *N,N*-diisopropylthioformamide with *N,N*-diisopropylselenoformamide, which we succeeded in preparing in analogous way as the sulfur compound. The spectra of these two compounds are as usual very similar, but the thioamide has a strong band at  $944 \text{ cm}^{-1}$  (shifted to lower frequencies on *S*-methylation or complex formation) which is missing in the spectrum of the selenium analogue; this has instead a medium strong band at  $816 \text{ cm}^{-1}$ , shifted to  $778 \text{ cm}^{-1}$  on *Se*-methylation.

It may be of interest to compare the spectra of the thioformamides and the corresponding formamides. Actually, they are rather similar in the  $1000\text{--}2000 \text{ cm}^{-1}$  range if it is accepted that the B band is comparable to the amide I band. Then formamide<sup>26</sup> has the amide II band at  $1608 \text{ cm}^{-1}$  comparable with the A band, the amide III band at  $1309 \text{ cm}^{-1}$  which is probably in this case quite comparable with our C band, and a band at  $1090 \text{ cm}^{-1}$  which probably corresponds to the  $1125 \text{ cm}^{-1}$  band of thioformamide. The strong  $\delta(\text{CH})$  vibration of formamide probably corresponds to the weak  $1288 \text{ cm}^{-1}$  band of thioformamide. The spectrum of *N,N*-dimethylformamide is also quite similar to that of *N,N*-dimethylthioformamide, except for the presence of the amide

I band and the B band, respectively. The infrared spectrum of *N*-methylformamide<sup>27</sup> is more different from that of *N*-methylthioformamide, especially because the "amide II band of secondary amides" has no exact counterpart in the spectra of thioamides. It is found at almost the same place as the B band of the thio compound, but, as discussed above, they can hardly be considered analogous. *N*-Methylformamide and *N,N*-dimethylformamide have no counterparts of the G bands of *N*-methylthioformamide and *N,N*-dimethylthioformamide, thus confirming that the assignments of these bands to CS stretching is correct.

*Thioacetamides.* The use of the formation of salts and complex compounds in the identification of the bands in the infrared spectrum of thioacetamide has been demonstrated by Kutzelnigg and Mecke,<sup>28</sup> who presented assignments for most of the frequencies observed. Later, Suzuki,<sup>7</sup> supplemented this work with observations of deuterated thioacetamide and showed that the application of the Urey-Bradley force field successfully explained the main features of the spectrum.

Recently, Collard-Charon and Renson<sup>15</sup> have investigated selenoacetamide in the range 900–1700 cm<sup>-1</sup>. They interpret their results to confirm the proposal set forth by Bellamy and Rogasch<sup>5</sup> that the strong band found at 975 cm<sup>-1</sup> in the spectrum of thioacetamide should be attributed chiefly to the CS group. However, the minor shift (to 955 cm<sup>-1</sup>) observed on going to selenoacetamide seems too small to warrant this conclusion. The band is weakened somewhat on *S*-protonation, *S*-methylation, or complex formation but only shifted slightly (either upwards or downwards) and is unchanged on deuteration. Accordingly, this band must essentially be due to a CH<sub>3</sub> vibration ( $\rho(\text{CH}_3)$ ), according to Kutzelnigg and Mecke<sup>28</sup>) with some slight contribution from a CS vibration. This is in accordance with the calculations by Suzuki,<sup>7</sup> who assigned the band to a combination of CC, CH<sub>3</sub>, and CS vibrations.

We have investigated the infrared spectra of thioacetamide and selenoacetamide in the range 400–4000 cm<sup>-1</sup>. In our opinion, the spectra should be considered practically identical in the range 800–4000 cm<sup>-1</sup>, no bands being shifted more than 20 cm<sup>-1</sup>. However, two notable changes were observed below 800 cm<sup>-1</sup>. The strong doublet, 706 + 718 cm<sup>-1</sup>, is replaced by two other bands at 716 cm<sup>-1</sup> and 615 cm<sup>-1</sup> when going from thioacetamide to selenoacetamide. We feel that the 615 cm<sup>-1</sup> band can, without doubt, be attributed to the CSe group; thus one of the bands in the doublet of thioacetamide must originate chiefly from the CS group. This is supported also by the calculation of Suzuki.<sup>7</sup> Furthermore, the doublet at 460 + 472 cm<sup>-1</sup> in the spectrum of thioacetamide has disappeared in the spectrum of selenoacetamide, which lends strong support to Suzuki's suggestion that this is due to a NCS deformation mode. Probably a new band found at 403 cm<sup>-1</sup> in the spectrum of selenoacetamide should be attributed to a skeletal vibration of the same kind.

The A, B, C, D, and F bands are easily identified in the spectrum of thioacetamide. According to Suzuki the 1482 cm<sup>-1</sup> band is chiefly associated with the  $\delta_a(\text{CH}_3)$  vibration (although with some coupling with the  $\nu(\text{CN})$  vibration); however, the shifts to higher frequencies on *S*-methylation, *S*-protonation, or formation of complex compounds are considerable, showing unambiguously that this band is a B band. The C band is affected similarly and weakened

Table 2. Infrared absorption bands ( $\text{cm}^{-1}$ ) of aliphatic dithio- and diselenoamides (in KBr).

Compound	A	B	C	D	E	F	G
<i>Dithioamide and derivatives.</i>							
$\text{CSNH}_2^*$	1582vs	1428s	1326m	1199m	—	699m	833s
$\text{CSNH}_2$							
$\left(\begin{array}{c} \text{CSNH}_2 \\   \\ \text{CSNH}_2 \end{array}\right) \text{CoCl}_2$	{ 1625w 1675w }	{ 1480vs 1520vs }	1400m	{ 1280m 1330w }	—	867s	770m
$\text{CSNHMe}^*$	—	{ 1540s 1550s }	1352s	1025s	—	{ 696s 875s }	—
$\text{CSNHMe}$	—	1520vs	{ 1490m 1248m }	1031s	—	{ 685vw 880vw }	—
$\left(\begin{array}{c} \text{CSNHMe} \\   \\ \text{CSNHMe} \end{array}\right) \text{CoCl}_2$	—	1520s	{ 1343m 1372m }	975m	—	{ 694m 879s }	—
$\text{CSNHCH}_2\text{Ph}$	—	1520s	1350m	1080m	—	{ 689m 900s }	—
$\text{CSNHCH}_2\text{COOH}$	—	1520s	{ 1339m 1389m }	1052s	—	{ 708m 820s }	—
$\text{CSNHCH}_2\text{CH}_2\text{OH}$	—	1515vs	1387m	976m	—	{ 705m 787m }	—
$\text{CSNHCH}_2\text{CH}_2\text{OH}$	—						
$\text{CSNHcyclohexyl}$	—						
$\text{CSNHcyclohexyl}$	—						

Table 2. Continued.

Compound	A	B	C	D	E	F	G
<i>Dithiomalonamide and derivatives.</i>							
$\text{H}_2\text{C}(\text{CSNH}_2)_2^*$	1625s	1445vs	1295m	{1215m, br {1235m, br	{965m {977s {990m	{721m {742s	799m
$[\text{H}_2\text{C}(\text{C}(\text{SMe})\text{NH}_2)_2]\text{I}_2$	1650m	1620vs	1400m	1200m	{1012m {1030w	731m	684m
$(\text{H}_2\text{C}(\text{CSNH}_2)_2)_2\text{CoCl}_2$	1610s	1500vs	1330s	1242m	1030w	730vw	796w
$\text{H}_2\text{C}(\text{CSeNH}_2)_2$	1630s	1452s	1281m	{1235m, br	{960m {972m	{735m {750m	766m
$\text{PhCH}(\text{CSNH}_2)_2$	1620s	1420vs	1308w	1020w	848w	778w	727s
$\text{PhCH}_2\text{CH}(\text{CSNH}_2)_2^*$	1625s	1420s	1268s	1128w	{798w {834m	{728m {770w	648s
$\text{Me}_2\text{C}(\text{CSNH}_2)_2^*$	1635s	1428s	1259m	1165m	904s	758m	700w
<i>Higher dithioamides.</i>							
$\text{CH}_2\text{CSNH}_2^*$	1625s	{1420vs {1440vs	{1280s {1232m	1150m	{978m {990s	764s	730s
$\text{CH}_2\text{CSNH}_2$	1640s	1435vs	1270s	1115m	{978m {1015s	766s	685m, br
$\text{CH}_2\text{CH}_2\text{CSNH}_2$							
<i>Dithiobiuret.</i>							
$\text{HN}(\text{CSNH}_2)_2^*$	{1620s {1640s	{1485s {1560vs	{1340vs {1395vs	{1230m, br {1270m, br	1120s	{725m {765m	{830m {837m
$\text{C}(\text{SMe})\text{NH}_2\text{I}$	1630m	{1500w {1600vs	{1308s {1390s	1200m, sh	1095w	{704m, sh {730m	823vw
$\text{PhCH}_2\text{CH}(\text{CSNH}_2)_2 \cdot 2\text{CuCl}$	{1600s {1615s	1560s, sh	1310m	—	830vw	—	625vw

considerably; it cannot therefore, be due to a  $\delta(\text{CH}_3)$  vibration as supposed by Kutzelnigg and Mecke.<sup>28</sup> The D band is only little influenced by *S*-methylation, and like the A, B, and C bands, is very little affected by selenation, but (in contrast to the B and C bands) very sensitive to deuteration. The F band is affected both by *S*-methylation and deuteration.

Collard-Charon and Renson<sup>15</sup> have assigned bands near 1100  $\text{cm}^{-1}$  in the spectra of *N*-methylthioacetamide and *N,N*-dimethylthioacetamide to the CS group but, for the reasons mentioned above, these assignments are considered incorrect. Rather, we assign the G band of *N*-methylthioacetamide to 680  $\text{cm}^{-1}$ , since this is shifted to a lower frequency on *S*-methylation. *N,N*-Dimethylthioacetamide has apparently two G bands (863 and 655  $\text{cm}^{-1}$ ) which are shifted to lower frequencies on selenation (to 834 and 606  $\text{cm}^{-1}$ , respectively) and *S*-methylation; however, the 655  $\text{cm}^{-1}$  band is probably comparable with the doublet at 460 + 472  $\text{cm}^{-1}$  in the spectrum of thioacetamide (see above). It seems to be a general rule that the bands due to C—S stretching and N—C—S deformation are found at considerably higher frequencies for tertiary than for secondary and primary amides, and an N—C—S deformation band may thus be found at such a high frequency that it may be confused with a G band. The D bands are tentatively assigned to 1100  $\text{cm}^{-1}$  and 1010  $\text{cm}^{-1}$  in these compounds. However, the skeletal vibrational nature of the D bands does not seem to be pronounced, as they are little affected by *S*-alkylation or selenation.

The spectra of higher primary thioamides — as examples, caprylic thioamide, palmitic thioamide and 2-phenylthioacetamide were investigated — show essentially the same features as the spectrum of thioacetamide (Table 1). The spectrum of cyanothioacetamide is more like that of dithiomalonamide, having a strong and broad D band.

*Higher N-methylthioamides.* Collard-Charon and Renson<sup>15</sup> have examined a series of secondary and tertiary thioamides in the range 900—2000  $\text{cm}^{-1}$  by selenation and deuteration. We have extended the range of investigation of some of these secondary amides to cover the region 400—900  $\text{cm}^{-1}$  and, on the basis of deuteration and alkylation studies, we assign the CS-vibration to ca. 700  $\text{cm}^{-1}$  in line with thioacetamide.

The spectra permitted an easy identification of the B, C, and D bands to about 1500  $\text{cm}^{-1}$ , 1400  $\text{cm}^{-1}$ , and 1000  $\text{cm}^{-1}$ , respectively. The deuterated spectra revealed some admixture of NH absorption in the B and C bands and proved the D bands to be due chiefly to the NH group. However, the F and G bands could not be located with certainty, as considerable coupling seems to occur in the 650—750  $\text{cm}^{-1}$  region.

The secondary thioamides examined all showed very strong and broad bands between 650 and 750  $\text{cm}^{-1}$ , whether the spectra were recorded of the thioamides as pure liquids or in solution. When the compounds were deuterated, these absorptions showed a general decrease in intensity, and at the same time a new pattern of well-defined bands appeared. This showed resemblance to the spectra of the *S*-methylated thioamides, except for the CS band, which was shifted toward lower frequencies. In this way the assignments of the G bands in the table were made, and the F bands were identified with the bands showing the most pronounced change on deuteration.

Table 3. Infrared absorption bands (cm<sup>-1</sup>) of aromatic and heteroaromatic thioamides and selenoamides (in KBr).

Compound	A	B	C	D	E	F	G
C <sub>6</sub> H <sub>5</sub> CSNH <sub>2</sub> *	1620vs	1400s	{1325m 1305w	1280m	—	689m	707m
[C <sub>6</sub> H <sub>5</sub> C(SMe)NH <sub>2</sub> ]I	1660s	1590s	{1320w 1305m	1268s	—	689s	680m
[C <sub>6</sub> H <sub>5</sub> C(SEt)NH <sub>2</sub> ]Cl	1650m,sh	1595vs,br	{1320w 1300w	{1270m 1275m	—	702m	685m
[C <sub>6</sub> H <sub>5</sub> C(SCH <sub>2</sub> COOH)NH <sub>2</sub> ]Br	1675s	1590s	{1325w 1305m	1275s	—	702m	690m,sh
(C <sub>6</sub> H <sub>5</sub> CSNH <sub>2</sub> )CuCl	1650s	1463s	{1320w 1307m	1261m	—	695vs,br	664m
C <sub>6</sub> H <sub>5</sub> CSeNH <sub>2</sub>	1624vs	1415m	{1320w 1309w	1261m	—	684m	664m
[C <sub>6</sub> H <sub>5</sub> (SeCH <sub>2</sub> COOH)NH <sub>2</sub> ]Br	1675s	1590vs	{1310vw 1300w	{1260s 1255s	—	700vw,br	—
C <sub>6</sub> H <sub>5</sub> CSNHMe *	—	1538vs	1359m	1045s	—	—	694s,sh
[C <sub>6</sub> H <sub>5</sub> C(SMe)NHMe]I	—	1585vs	1415m	1016m	—	—	678m
C <sub>6</sub> H <sub>5</sub> CSNMe <sub>3</sub>	—	1533s	1395s	1137s	—	—	989w
[C <sub>6</sub> H <sub>5</sub> C(SMe)NMe <sub>2</sub> ]I	—	1623vs	1400w	1152m	—	—	935w
C <sub>6</sub> H <sub>5</sub> CSeNMe <sub>3</sub>	—	1539s	1390s	1128s	—	—	944m
[C <sub>6</sub> H <sub>5</sub> C(SeMe)NMe <sub>2</sub> ]I	—	1622vs	1400w	1144m	—	—	931m
C <sub>6</sub> H <sub>5</sub> CSNHC <sub>6</sub> H <sub>5</sub> *	—	1530s	1360s	{983m 998w	—	767m	708s
(C <sub>6</sub> H <sub>5</sub> CSNHC <sub>6</sub> H <sub>5</sub> )CuCl	—	1520vs	1405s	999s	—	775s	<670
<i>p</i> -Bu <sup>14</sup> OC <sub>6</sub> H <sub>4</sub> CSNHMe	—	1525vs	1335m	1030s	—	830s	728m
<i>p</i> -Bu <sup>14</sup> OC <sub>6</sub> H <sub>4</sub> CSNHCMe <sub>3</sub>	—	1515s	1360s	990s	—	835s	732m
<i>o</i> -C <sub>6</sub> H <sub>4</sub> (OH)CSNH <sub>2</sub> *	{1639s 1614s	1473s	1320s	1230s	895s	757s	742m
( <i>o</i> -C <sub>6</sub> H <sub>4</sub> (O)SNH)Ni	—	1555m	1310m	1240s	900vw	755s	706w
3-C <sub>6</sub> H <sub>3</sub> N-CSNH <sub>2</sub> * (thionicotinamide)	1680s	1459s	1310m	1150m	918s	770m,br	{701s 710m,sh
3-C <sub>6</sub> H <sub>3</sub> NCSNH <sub>2</sub> ·HCl	{1640m 1625sh	1525s	1300s	{1140vw 1150vw	{920m 895w 885w	{772m 790w	{675s 690m
3-C <sub>6</sub> H <sub>3</sub> N <sup>+</sup> H·CSNH <sub>2</sub> ·CuCl <sub>2</sub> <sup>-</sup>	1650s	1540m	1308m	1142w	900s	752w,br	677m
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CSNH <sub>2</sub>	1625s	1417m	1320m	1250w	948m	{788s 735s	732s
(C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CSNH <sub>2</sub> )CuCl	1625s	1530w	1340w	1280m	940vw	{760w 728m	642w
[C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> C(SMe)NH <sub>2</sub> ]I	1650s	1530w	1402s	1280w	—	{750m 725w	—

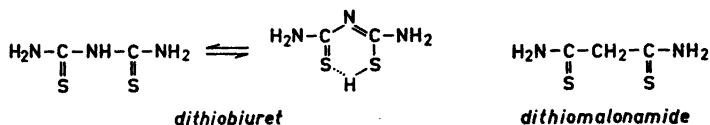
*Dithioamides.* The infrared spectrum of dithiooxamide (rubeanic acid) has been investigated by Scott and Wagner<sup>29</sup> in the range 400–4000  $\text{cm}^{-1}$ . By comparison with oxamide and the deuterated species, assignments were made for the vibrational modes which were found consistent with the observed physical properties. The overall results show good agreement with the changes observed in the spectra on complex formation (Table 3) reported here. It is noteworthy that the A band at 1582  $\text{cm}^{-1}$  due to the amino group shows a splitting when going from dithiooxamide to the cobalt(II) chloride complex or to the methyl iodide adduct. The reason for this might well be of a steric nature as no comparable effect is found for the higher thioamides, *e.g.* dithiomalonamide. Furthermore, the assignment of the strong band at 833  $\text{cm}^{-1}$  to the CS group is chiefly supported by the shift to lower frequencies which reflects the diminished double-bond character induced by complex formation through the sulfur atom. The shoulder at 1326  $\text{cm}^{-1}$  in dithiooxamide was not discussed by Scott and Wagner; however, the shifts observed on methylation (1400  $\text{cm}^{-1}$ ) obviously characterises it as the C band.

While the *N,N'*-disubstituted dithiooxamides all exhibit easily recognizable B, C, and D bands the F bands seem to be doubled. This may be inferred from the replacement of the band near 700  $\text{cm}^{-1}$  as well as the band found in the 800–920  $\text{cm}^{-1}$  range in the deuterated compounds. In *N,N'*-dimethyldithiooxamide, a new band appeared at 731  $\text{cm}^{-1}$  on deuteration which could be ascribed to the CS group in analogy with the corresponding band identified in deuterated dithiooxamide<sup>29</sup> at 746  $\text{cm}^{-1}$ . However, these conclusions are useless for analytical purposes and we have thus omitted such assignments from the table.

We have prepared diselenomalonamide with a view to locating the position of the CS-vibration in dithiomalonamide. Only very small variations in intensity and position could be detected when these patterns were compared except for the shift of a weak to medium intensity band in dithiomalonamide at 799  $\text{cm}^{-1}$  to 766  $\text{cm}^{-1}$  in diselenomalonamide and the appearance of a new band at 1515  $\text{cm}^{-1}$  in some samples of the latter compound. While the origin of the 1515  $\text{cm}^{-1}$  band is obscure, we attribute the peak at 799  $\text{cm}^{-1}$  in dithiomalonamide to the CS group. This correlation is further confirmed by the shift to lower frequencies (possibly 684  $\text{cm}^{-1}$ ) found on the addition of methyl iodide and the minor change of position on deuteration. Attempts to oxidise diselenomalonamide to the corresponding cyclic diselenolyl salt, as reported for dithiomalonamide by Jensen, Baccaro and Buchardt,<sup>30</sup> were unsuccessful.

The pattern of the infrared spectrum of dithiobiuret is much like that of dithiomalonamide, except that much doublet splitting has occurred. As discussed earlier,<sup>30</sup> this doubling disappears when dithiobiuret is oxidized to the dithiazolyl cation. The infrared spectrum shows weak bands which indicate that dithiobiuret partly exists in its tautomeric thiol form (SH band at 2600  $\text{cm}^{-1}$ , C=N shoulder at 1660  $\text{cm}^{-1}$ ), which may explain the presence of doublet absorption peaks. The NMR-spectrum is consistent with this proposal, as 3 single bands are found in DMSO in the intensity ratio 1:2:2, ( $\tau = -0.67$ ,  $+0.45$ , and  $+0.83$ , resp.). This definitely rules out the simple dithioamide structure, and suggests nearly complete conversion to the thiol form. Tautomerism is less likely in the case of dithiomalonamide:





*Aromatic thioamides.* The attachment of an aromatic nucleus to the thioamide grouping appears to be of only minor influence on the position of the characteristic bands (Table 3). Irrespective of the great number of bands in the spectra arising from the benzene nucleus, a systematic study involving selenation, deuteration, complexing, and alkylation served to identify the 6 bands which are expected for the thioamide grouping in thiobenzamide. In the 1200–1700  $\text{cm}^{-1}$  range a total of eight bands was found, of which the three bands at 1449  $\text{cm}^{-1}$ , 1490  $\text{cm}^{-1}$ , and 1593  $\text{cm}^{-1}$  could be attributed unambiguously to the phenyl group on the basis of the above-mentioned investigations. The remaining 5 bands are considered to be the A, B, C, and D bands, the C band apparently showing a splitting. From the table it can be seen, that while the A and B bands behave normally, the C and D bands are, to a certain degree, unaffected by the classification tests. Deuteration proved both bands to possess some NH-character, but their origins are still in doubt.

The F and G bands were identified by a comparison of the deuterated and the selenated compounds.

Thiobenzamide has a strong band at 885  $\text{cm}^{-1}$  which is unaffected by deuteration but shifted slightly on complex formation (872s) or *S*-alkylation with methyl iodide (862s), ethyl chloride (870s) or bromoacetic acid (860m, 900m). Selenobenzamide has a corresponding band at 835  $\text{cm}^{-1}$ (s). However, the infrared spectra of *S*-carboxymethylthiobenzamidium bromide and *Se*-carboxymethylselenobenzamidium bromide are practically identical in the 800–900  $\text{cm}^{-1}$  range whereas they differ very much in the 600–700  $\text{cm}^{-1}$  range; the assignment of the G band of thiobenzamide to 707  $\text{cm}^{-1}$  rather than to 885  $\text{cm}^{-1}$  is therefore undoubtedly correct.

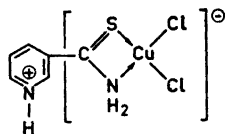
The shift of the D band from 1280  $\text{cm}^{-1}$  to 1045  $\text{cm}^{-1}$  when going from thiobenzamide to the *N*-methyl derivative parallels the behaviour of thioacetamide. The doublet at 687  $\text{cm}^{-1}$  and 694  $\text{cm}^{-1}$  in *N*-methylthiobenzamide probably consists of the G band together with the phenyl group absorption ordinarily found at this place in the spectrum. In support of this, the G band is lowered to 678  $\text{cm}^{-1}$  on methylation with methyl iodide, while the phenyl absorption is shifted to 705  $\text{cm}^{-1}$ . Deuteration leaves the range 670–800  $\text{cm}^{-1}$  unchanged, thus the F band must be placed below this range. The superposition of the spectra of *N,N*-dimethylthiobenzamide and the selenoanalogue proved the G bands to be located at 989  $\text{cm}^{-1}$  and 944  $\text{cm}^{-1}$ , respectively. The methylated compounds showed the expected shifts to 935  $\text{cm}^{-1}$  and 931  $\text{cm}^{-1}$ , respectively, as well as an upwards shift (10  $\text{cm}^{-1}$ ) of the peaks due to the benzene ring at *ca.* 700  $\text{cm}^{-1}$  and 760  $\text{cm}^{-1}$ .

The identification of the B, C, and D bands in more complicated derivatives of thiobenzamide presented no difficulties; however, the F and G bands, believed to be located in the range 670–900  $\text{cm}^{-1}$ , were intimately mixed.

In thiobenzanilide, four bands could be seen in this range, at 689, 708, 752, and 767  $\text{cm}^{-1}$ , of which the 689  $\text{cm}^{-1}$  band undoubtedly arises from a phenyl group vibration. The remaining three bands are considered due to mixed vibrations of the phenyl groups, the CS group, and the NH group; thus the assignments in the table cannot be used rigorously.

The infrared spectra of thiobenzanilide and some similar secondary thioamides have also been investigated by Hadzi.<sup>2</sup> However, we do not agree with this author that the "thioureide band" of these compounds is comparable with the amide II band of secondary amides. The band does not disappear on deuteration but is only shifted to a slightly lower frequency.

The infrared spectrum of 3-pyridinethiocarboxamide (thionicotinamide) is abnormal in so far as the A band is found at an unusually high frequency (1680  $\text{cm}^{-1}$ ) which is lowered on formation of a copper(I) chloride complex. The reason for this behaviour is found in the presence of a pronounced SH band at 2570  $\text{cm}^{-1}$  in the spectrum of thionicotinamide, indicating that this thioamide has the tautomeric thiol structure. On the complex formation, or addition of hydrochloric acid, the SH band disappears. The complex has the composition of a thiocarboxamidopyridinium dichlorocuprate(I),  $\text{H}_2\text{NCS}-\text{C}_5\text{H}_5\text{NH}^+\text{CuCl}_2^-$ ; the shifts of the bands on formation of the complex from the hydrochloride show, however, that the dichlorocuprate(I) ion is attached to the thioamide grouping so that the structure of the complex may be written:



In 2-hydroxythiobenzamide, the splitting of the A band (1614  $\text{cm}^{-1}$  and 1639  $\text{cm}^{-1}$ ) as well as the presence of a broad band at 2600–2800  $\text{cm}^{-1}$  indicates the occurrence of intramolecular hydrogen bonding. This compound further has an E band at 895  $\text{cm}^{-1}$  and an OH deformation band at 1385  $\text{cm}^{-1}$ . On deuteration or formation of a nickel complex all these bands disappear. The absence of not only the OH band but also the A band in the spectrum of the nickel compound, as well as its analytical composition (ligand-metal ratio 1:1) indicates that it is derived from the doubly charged phenolate-thioamidate anion of *o*-hydroxythiobenzamide. The B band was identified by a shift from 1473 to 1555  $\text{cm}^{-1}$  and the G band by a shift from 742 to 706  $\text{cm}^{-1}$  when the thioamide was transformed into the nickel compound.

*Thiopiperidides.* The thiopiperidides prepared in an earlier work<sup>31</sup> all show very strong B bands near 1500  $\text{cm}^{-1}$  which move to *ca.* 1600  $\text{cm}^{-1}$  on *S*-alkylation with methyl iodide or bromoacetic acid (Table 4). Some morpholides and piperazides studied by Goulden<sup>32</sup> and Guépet *et al.*<sup>33</sup> behave in the same way. On *S*-alkylation the CN bond attains considerable double-bond character without, however, reaching the normal C=N vibration frequency. The lower values found can, of course, be attributed to resonance contribution from the sulfonium form to the predominating ammonium form of the cation.

Table 4. Infrared absorption bands ( $\text{cm}^{-1}$ ) of thiopiperidides and thiopiperididium salts.

Compound		B	C	D	G
HCSNC <sub>5</sub> H <sub>10</sub>	(CCl <sub>4</sub> )	1500vs	1275m	{1135m 1110m	912m
[HC(SMe)NC <sub>5</sub> H <sub>10</sub> ]I	(KBr)	1630vs	1310m	{1140w 1090m	875m
CH <sub>3</sub> CSNC <sub>5</sub> H <sub>10</sub>	(KBr)	1500vs	1257s	1052s	657m
[CH <sub>3</sub> C(SMe)NC <sub>5</sub> H <sub>10</sub> ]I	(KBr)	1597vs	1275w	—	643m
[CH <sub>3</sub> C(SCH <sub>2</sub> COOH)NC <sub>5</sub> H <sub>10</sub> ]Br	(KBr)	1610s	1275w	—	—
(CH <sub>3</sub> ) <sub>3</sub> C-CSNC <sub>5</sub> H <sub>10</sub>	(KBr)	1423vs	1249s	{1109m 1131s	785w
[(CH <sub>3</sub> ) <sub>3</sub> C-C(SMe)NC <sub>5</sub> H <sub>10</sub> ]I	(KBr)	1550vs	1239m	{1094m 1134w	777w
C <sub>6</sub> H <sub>5</sub> CSNC <sub>5</sub> H <sub>10</sub>	(KBr)	1492s	1200m	{1105w 1136m	677w
[C <sub>6</sub> H <sub>5</sub> C(SMe)NC <sub>5</sub> H <sub>10</sub> ]I	(KBr)	1587vs	1195w	{1092w 1135vw	667vw
<i>p</i> -MeO-C <sub>6</sub> H <sub>4</sub> CSNC <sub>5</sub> H <sub>10</sub>	(KBr)	1487s			
[ <i>p</i> -MeO-C <sub>6</sub> H <sub>4</sub> C(SCH <sub>2</sub> COOH)NC <sub>5</sub> H <sub>10</sub> ]Br	(KBr)	1604s			
<i>o</i> -MeO-C <sub>6</sub> H <sub>4</sub> CSNC <sub>5</sub> H <sub>10</sub>	(KBr)	1484vs		not identified	
<i>m</i> -ClC <sub>6</sub> H <sub>4</sub> CSNC <sub>5</sub> H <sub>10</sub>	(KBr)	1493vs			
[ <i>o</i> -Pr <sup>1</sup> O-C <sub>6</sub> H <sub>4</sub> C(SCH <sub>2</sub> COOH)NC <sub>5</sub> H <sub>10</sub> ]Br	(KBr)	1608s			
[ <i>o</i> -Bu <sup>1</sup> O-C <sub>6</sub> H <sub>4</sub> C(SCH <sub>2</sub> COOH)NC <sub>5</sub> H <sub>10</sub> ]Br	(KBr)	1603s			
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>2</sub> CSNC <sub>5</sub> H <sub>10</sub>	(KBr)	1494vs			

According to Goulden,<sup>32</sup> quaternization may lead to a decrease in the value of the C=N frequency. However, the author came to this conclusion by comparing the quaternary ion, C<sub>6</sub>H<sub>5</sub>-C(SCH<sub>3</sub>)=N<sup>+</sup>(CH<sub>3</sub>)C<sub>6</sub>H<sub>5</sub>, with the thioimide C<sub>6</sub>H<sub>5</sub>-C(SCH<sub>3</sub>)=NC<sub>6</sub>H<sub>5</sub> rather than with the corresponding ternary cation C<sub>6</sub>H<sub>5</sub>-C(SCH<sub>3</sub>)=N<sup>+</sup>HC<sub>6</sub>H<sub>5</sub>. The latter has the B band in almost the same place (1555  $\text{cm}^{-1}$ ) as the quaternary ion (1562  $\text{cm}^{-1}$ ). The CN bond in the thioimide, on the other hand, is almost a normal double bond, because a sulfonium form with a negatively charged nitrogen atom can evidently make very little contribution to the structure. Therefore, the C=N frequency is nearer to that of a normal C=N bond; the frequency is lowered by the formation of a cation and not specifically by quaternization. An analogous lowering of the double-bond frequency (near 1700  $\text{cm}^{-1}$ ) is not observed when imidic esters are transformed into their hydrochlorides, because there will be no significant contribution from the oxonium structure even in the cations.

The C and D bands in the spectra of thiopiperidides could, in most cases, be identified near 1250 and 1100  $\text{cm}^{-1}$ , respectively. They shift to higher frequencies on *S*-alkylation. The G band, which is characterized by shifting to lower frequencies on *S*-alkylation, is located below 800  $\text{cm}^{-1}$ , except for thioformylpiperidine (*cf.* the thioformamides).

## INFRARED SPECTRA OF THIOUREAS

This class of compounds has not been studied very extensively,\* with the exception of the first member, thiourea. Stewart's assignments for thiourea<sup>21</sup> are largely incorrect and should be replaced by the more realistic approach of Yamaguchi *et al.*,<sup>4,34</sup> who have based their discussion on the concept of mixed vibrations. However, as already pointed out in the discussion of the characteristic bands, our experimental results do not in all cases support the assignments of Yamaguchi *et al.*<sup>4</sup> The discrepancies are especially connected with the question of the degree of contribution of the CS stretching vibration to the various bands.

We have tried to solve some of these difficulties by a comparative study of the spectra of thioureas and selenoureas. Independently, Collard-Charon and Renson<sup>20</sup> have made a similar comparative study of thioureas and selenoureas. However, these authors assign the band at 1086  $\text{cm}^{-1}$  in the spectrum of thiourea to the CS group, whereas we suggest a considerable lower frequency (629  $\text{cm}^{-1}$ ), primarily on the basis of the absence of the counterpart of this band in the spectrum of selenourea. This was not noted by Collard-Charon and Renson because of the limitation of the range investigated; consequently, this method is only safe in full-range investigations. The peak found at 629  $\text{cm}^{-1}$  is shifted to 592  $\text{cm}^{-1}$  in the spectrum of *S*-methylthiuronium iodide and to *ca.* 550  $\text{cm}^{-1}$  in the spectra of complex compounds of thiourea, which also characterizes it as a G band. The presence of a band due to the CSe group could not be ascertained for selenourea, as there is a broad band of medium intensity covering the 520–600  $\text{cm}^{-1}$  range. However, the location of the G band in the spectra of substituted selenoureas usually presented no difficulties.

It has been concluded<sup>4</sup> that the lowering of the 727  $\text{cm}^{-1}$  band of thiourea on formation of complex compounds with metal halides should be attributed to the reduced double bond character of the CS bond following complex formation and therefore does support the assignment of this band to the C=S group. However, this band can, at most, share some CS character because deuteration causes a splitting of it into a weak band at 690  $\text{cm}^{-1}$  and a medium intensity band at 670  $\text{cm}^{-1}$ , while methylation produces a small shift to 732  $\text{cm}^{-1}$  in the opposite direction of that expected for a CS frequency. From the point of view adopted here, this band is obviously best characterized as the F band. This is also supported by its absence in the spectra of tetrasubstituted thioureas. If this band is in part due to a torsional NH vibration, it is conceivable that the frequency should be lowered as a consequence of increased double bond character of the CN bond.

Swaminathan and Irving<sup>35</sup> have recently criticized the results of Yamaguchi *et al.*<sup>4</sup> on the infrared spectra of metal complexes of thiourea and claim that the differences between the infrared spectrum of thiourea itself and those of its metal complexes are confined to two bands only (our C and G band). However, our results with  $[\text{Pt}(\text{tu})_4]\text{Cl}_2$  have fully confirmed the results of Yamaguchi *et al.* that complex formation may increase the frequency of the

\* However, infrared absorption bands have been reported for several substituted thioureas,<sup>1,20,22,36,54,55</sup> especially in the 1500–1600  $\text{cm}^{-1}$  range.<sup>54</sup>

Compound	A	B	C	D	E	F	G
Thiourea *	1612vs	1473s	1413vs	1086s	—	727m	629m
Selenourea	1610vs	1488m	1407s	1090w	—	735w	—
Thiourenium chloride *	1660vs	1540vw	{1398m 1439m}	1085vw	—	{702vw 725vw}	not inv.
S-Methylthiourenium iodide	1638vs	1520w	1425m	{1063vw 1100vw}	—	727vw	592w
S-Methylthiourenium sulfate	1644s	1564w	1443s	hidden	—	732m	not inv.
S-Benzylthiourenium chloride	1625s	1550w	1420m	{1073w 1098w}	—	725w	—
[Pt(H <sub>2</sub> N - CS - NH <sub>2</sub> ) <sub>4</sub> ]Cl <sub>2</sub>	{1605s 1625s}	1504m	{1385s 1425s}	1080w	—	706m	{637m 562m}
[Cu(H <sub>2</sub> N - CS - NH <sub>2</sub> ) <sub>2</sub> ]Cl	{1610s 1635s}	1500w	{1385s 1420m}	1090m,br	—	706m	530m,br
N-Methylthiourea *	1627s	{1550vs 1562s}	{1257s 1297m}	{1125m 1148m}	777m	719s	625m
[Pt(MeNH - CS - NH <sub>2</sub> ) <sub>4</sub> ]Cl <sub>2</sub>	{1617s 1635s}	1569s	{1245m 1285s}	{1125m 1145m}	{763m 773m}	719m	{607m 637m}
N,S-Dimethylthiourenium iodide	1640vs	1600vs	1295m	{1122m 1158m}	776w	720w,br	not inv.
N-Methylselenourea	1633vs	1562vs	1278s	{1120m 1150m}	735m,sh	722m	602m
N-Ethylthiourea *	1625vs	{1548vs 1567vs}	{1267m 1308m}	{1112w 1130m}	807m	740m	644m
[Pt(EtNH - CS - NH <sub>2</sub> ) <sub>4</sub> ]Cl <sub>2</sub>	1627vs	{1562s 1582s}	{1267s 1303m}	1123m	790w	743w	628m
N-Ethyl-S-methylthiourenium iodide (in CHCl <sub>3</sub> )	1635vs	1590m	1230m,br	1159m	819m	hidden	624w,br
N-Ethylselenourea	1631vs	{1531vs 1549m}	{1265m 1299w}	{1113m 1145w}	750m	737m	591m
N-Ethyl-Se-methylselenourenium iodide	1635vs	1580vs	1260s	1116m	750w	705w	550w,br
N-Isopropylthiourea	1622s	1562vs	1356s	{1129w 1176s}	866w	{700m 722m}	not inv.
N-Butylthiourea	1619vs	1562vs	1356s	1164m	—	726m	not inv.
N-Butylselenourea *	1620vs	1550vs	1345w	1135m	—	731m	not inv.
N-(α-Methyl)thiourea	1620s	1565s	1350s	1159m	—	724m	not inv.
N-(β-Methyl)thiourea	1632s	{1535s 1550s}	1318s	1127m	—	733m	not inv.
N-Hexylthiourea	1620s	1565s	1349s	1162m	—	710m,sh	not inv.
N-Phenylthiourea *	1610s	{1520s 1530s}	1312m	{1060m 1072w}	810m	714m	not inv.
S-Methyl-N-phenylthiourenium iodide	1625vs	1565s	1377m	1065m	—	718m	not inv.
S-Methyl-N-phenylisothiourea	1620s	1570vs	{1282s 1290s}	—	{829m 837m}	718m	not inv.
N-(o-Chlorophenyl)thiourea	1615s	1549s	1322m	1058m	—	{720m 728m}	not inv.

A, B, C, and also the D bands. This is also what would be expected for reactions which increase the double bond character of the CN bond (incidentally, the A band is not due to a pure  $\text{NH}_2$  vibration and the C band certainly not to C—S stretching as maintained by Swaminathan and Irving). The increase in frequency of the A, B, C, and D bands is very conspicuous on *S*-protonation and *S*-methylation, but is incontestable also in the spectra of many complexes, e.g. the nickel-thiourea complexes studied by Olliff,<sup>36</sup> the  $\text{SnCl}_4$  and  $\text{SnBr}_4$  complexes of thiourea,<sup>37</sup> and as a matter of fact, also in the spectra of the copper, cadmium, and mercury complexes published by Swaminathan and Irving. As would be expected, it is only weakly coordinated metal ions such as  $\text{Mn}^{2+}$ ,  $\text{Pb}^{2+}$ , etc. which do not influence the A, B, and D bands perceptibly.

The changes of the spectrum of thiourea on *S*-protonation, *S*-methylation, and complex formation lend support to the view that the B, C, and D bands have their origin mainly in the  $\nu_{\text{as}}(\text{N—C—S})$ ,  $\nu(\text{N—C—N})$ , and  $\nu_{\text{s}}(\text{N—C—S})$  vibrations, respectively. However, as shown below, considerable coupling with NH vibrations occur in substituted thioureas with secondary NH groups. The F and G bands are mainly due to NH and CS vibrations, respectively, as discussed above.

*Monosubstituted thioureas.* The strong, characteristic A and B bands were easily recognized in the infrared spectra of the monosubstituted thioureas investigated. Deuteration studies proved the A band to be essentially due to the amino group, while the B band, occasionally occurring as a strong doublet, was rather unaffected by this treatment, as in thiourea. The C band could, in all cases, be identified as the strongest band in the 1200—1400  $\text{cm}^{-1}$  range. Being essentially a composite band, deuteration caused separation of the N—D frequencies and the appearance of a strong band at, or just below, 1400  $\text{cm}^{-1}$ , paralleling the strong band in tetradeuterio-thiourea at 1380  $\text{cm}^{-1}$ . As the C band is not sensitive to *S*-alkylation, this component must, therefore, be due to the N—C—N grouping chiefly. The D band is the strongest band in the 1000—1200  $\text{cm}^{-1}$  range, occurring at slightly higher frequencies in the aliphatic (1125—1175  $\text{cm}^{-1}$ ) than in the aromatic (ca. 1060  $\text{cm}^{-1}$ ) thioureas, and assigned to the NH group (deuteration). The presence of an E band could only be ascertained in some of the lower thioureas, in the higher members of this series it must be very weak, if present. The F band is only of analytical interest for the aliphatic thioureas, being obscured by the phenyl group absorptions in the aromatic compounds, in which its presence could only be detected through deuteration studies. The G band, in so far it has been sought for, was found in the range 625—650  $\text{cm}^{-1}$  as for thiourea (629  $\text{cm}^{-1}$ ). The criteria used for identification were the same as for thiourea.

*Asymmetrically disubstituted thioureas.* The general features of the few members investigated of this group (Table 6) are only to a small extent different from the monosubstituted thioureas. Thus the C bands are, contrary to the former group, unaffected by deuteration which indicates that the NH-character of the C bands in the monosubstituted thioureas originates from the secondary thioamide grouping. The F band may be of analytical interest since it is located below 700  $\text{cm}^{-1}$  in the *as*-disubstituted, but in the range 700—750  $\text{cm}^{-1}$  in the monosubstituted thioureas. This, together with the presence of the A band, helps to distinguish these compounds.

Table 6. Infrared absorption bands ( $\text{cm}^{-1}$ ) of symmetrically disubstituted thioureas and selenoureas (in KBr).

Compound	B	C	D	F	G
<i>N,N'</i> -Dimethylthiourea *	1565vs	{ 1260s 1287s	{ 1016m 1040s	720m	637m
<i>N,N',S</i> -Trimethylthiuronium iodide	1618vs	1275m	1036s	731w	<625
<i>N,N'</i> -Dimethylselenourea	1560vs	{ 1260m,sh 1281m	{ 990w 1029m	700vw	605m
<i>N</i> -Methyl- <i>N'</i> -ethylthiourea	{ 1550vs 1565vs	1259s	{ 1025s 1038m	759w	not inv.
<i>N</i> -Methyl- <i>N'</i> - <i>tert</i> -butylthiourea *	{ 1530vs 1550vs	1279s	{ 1020m 1042w	774m	not inv.
<i>N</i> -Methyl- <i>N'</i> -cyclohexylthiourea	{ 1545vs 1560vs	1279m	1020m	755m	not inv.
<i>N</i> -Methyl- <i>N'</i> -benzylthiourea	{ 1552s 1570vs	1280m	{ 1027w 1065m	767m	not inv.
<i>N</i> -Methyl- <i>N'</i> -( $\alpha$ -methylbenzyl)-thiourea	{ 1550vs 1570vs	1332s	1042m	763m	not inv.
<i>N</i> -Methyl- <i>N'</i> -phenylthiourea	{ 1530vs 1550vs	1281s	{ 1020m 1047w	774m	636m
<i>N,N'</i> -Diethylthiourea *	1560vs	1240vs	1052m	798m	645m
[Pt(EtNH—CS—NHEt) <sub>4</sub> ]Cl <sub>4</sub>	{ 1576vs 1590vs	1250s	{ 1035w,sh 1050m	792m	635m
<i>N,N'</i> -Diisopropylthiourea	1560vs	{ 1240s 1255s	980m	—	740m
<i>N,N'</i> -Diisopropyl- <i>S</i> -methylthiuronium iodide	1600vs	1272m	{ 972m 1000m	—	—
<i>N,N'</i> -Diisopropylselenourea	1565vs	1262s	973s	—	667m,sh
<i>N,N'</i> -Diisopropyl- <i>Se</i> -methylselenouronium iodide	1592vs	1262s	969w	—	—
<i>N</i> -Allyl- <i>N'</i> - <i>p</i> -carboxyphenylthiourea	1535vs	{ 1291s 1304s	—	{ 764m 789w	not inv.
<i>N,N'</i> -Dibutylthiourea	1570vs	{ 1218m 1248m	1079m	{ 768m 798m	not inv.

Table 6. *Continued.*

Compound	B	C	D	F	G
<i>N</i> -Butyl- <i>N'</i> - <i>tert</i> -butylthiourea	{1535vs 1550vs}	1340vs	1087m	{738w 785w 731m 740m}	not inv. not inv.
<i>N</i> -Butyl- <i>N'</i> -phenylthiourea	1552vs	*1234s	1066m	768m	not inv.
<i>N</i> -Hexyl- <i>N'</i> -phenylthiourea	{1552vs 1565s}	1318s	{1073m 1080m}	—	771m 759w
<i>N,N'</i> -Dicyclohexylthiourea *	1553vs	1230m	982m	—	735m
<i>N,N'</i> -Dicyclohexyl- <i>S</i> -methylthiouronium iodide	1600vs	1238w	979m	—	732w
<i>N,N'</i> -Dicyclohexylselenourea *	{1551vs 1559vs}	1229m	975m	—	629m
<i>N,N'</i> -Dicyclohexyl- <i>Se</i> -methylselenouronium iodide	1601vs	1239w	975m	{754m 763w 748s 763w}	559s
<i>N,N'</i> -Diphenylthiourea *	1551vs	1345s	—	744m	not inv.
<i>N,N'</i> -Diphenylselenourea	1551vs	{1320s 1335s}	—	762m	not inv.
<i>N</i> -Phenyl- <i>N'</i> -benzylthiourea *	{1530vs 1540vs}	1240s	—	753m	not inv.
<i>N</i> -Phenyl- <i>N'</i> - <i>o</i> -tolylthiourea	1528s	1260s	—	766m	not inv.
<i>N</i> -Phenyl- <i>N'</i> - <i>p</i> -tolylthiourea	1548s	1241s	—	—	not inv.
<i>N</i> -Phenyl- <i>N'</i> - <i>p</i> -bromophenylthiourea	1551vs	{1240m 1333s}	—	—	not inv.
<i>N</i> -Phenyl- <i>N'</i> - $\beta$ -naphthylthiourea	1551vs	{1242m 1344s}	—	759m	not inv.
<i>N,N'</i> -Di- <i>o</i> -tolylthiourea	1523vs	1262s	—	769m	not inv.
<i>N,N'</i> -Di- <i>p</i> -tolylthiourea	1551s	1247s	—	{761m 773w}	not inv.



*Symmetrically disubstituted thioureas.* In these compounds the A and E bands are absent in accordance with the substitution at both nitrogen atoms. Furthermore, the D band is absent or very weak in symmetrically aromatic disubstituted thioureas, a feature also found in the asymmetrically disubstituted thioureas.

The location of the B, C, D, and F bands presented no difficulties for this group. However, in the aromatic compounds the F bands occur in the close vicinity of the phenyl group absorptions, and thus are dubious and of only little analytical interest. While the B bands are unaffected by deuteration, the C bands were shifted to the 1350–1400  $\text{cm}^{-1}$  region, thus considerable NH character seems to be present in these vibrations. It should be noted, that this is analogous to the behaviour of the monosubstituted thioureas, and therefore it appears that the NH-character in the C bands originates from a secondary amino group.

*Trisubstituted thioureas.* The location of the characteristic bands in the spectra of these compounds presented no difficulties. As expected, the C band proved to be composite, as deuteration caused the main peak to shift towards 1400  $\text{cm}^{-1}$ . From the results obtained, there seems to be a definite tendency for the D band to be found in the range 1100–1150  $\text{cm}^{-1}$  if the NH group is linked to an aromatic nucleus, but below 1100  $\text{cm}^{-1}$  if the neighbouring group is aliphatic; however, further investigations are necessary to settle this proposal. It is interesting to find the F band in trimethylthiourea at 900  $\text{cm}^{-1}$ , which is far beyond the range expected (650–800  $\text{cm}^{-1}$ ); however, it is doubled on deuteration and no other absorptions could be detected in the region 670–900  $\text{cm}^{-1}$ . As a corresponding band is found for tetramethylthiourea, we assign this peak to a mixture of methyl and NH vibrations; this also accounts for the splitting observed in the spectrum of *S*-benzyl-trimethylthiuronium chloride (866 + 898  $\text{cm}^{-1}$ ). In so far as the G band was sought for it was found in the usual range.

Assignment of the G band by means of selenation was made for *N,N,N'*-trimethylthiourea and *N,N*-dipropyl-*N'*-cyclohexylthiourea. Although the infrared spectrum of the last-mentioned compound shows several bands in the 600–800  $\text{cm}^{-1}$  range a comparison of its spectrum with that of the corresponding selenourea shows unambiguously that the 716  $\text{cm}^{-1}$  band is the G band because it is shifted to 623  $\text{cm}^{-1}$  in the spectrum of the selenourea while three other bands (746, 685, 643  $\text{cm}^{-1}$ ) remained almost unchanged in position and shape when going to the selenourea.

There was a corresponding shift of a band at 587  $\text{cm}^{-1}$  to 525  $\text{cm}^{-1}$  when going from this thiourea to the corresponding selenourea (and replacement of two bands at 595  $\text{cm}^{-1}$  and 546  $\text{cm}^{-1}$  by a band at 523  $\text{cm}^{-1}$  in the case of trimethylthiourea); tentatively these bands are assigned to the N–C–S and N–C–Se deformation modes, *cf.* the bands found in the same range for thioacetamide.

*Tetrasubstituted thioureas.* The infrared spectra of tetrasubstituted thioureas are unusual in so far as they are almost identical in the 1000–4000  $\text{cm}^{-1}$  range with the spectra not only of the corresponding selenoureas, but also of the corresponding ureas, except for the absence of the strong C=O band, found near 1650  $\text{cm}^{-1}$  in the spectra of tetrasubstituted ureas. This indicates

Table 7. Infrared absorption bands ( $\text{cm}^{-1}$ ) of asymm. disubstituted thioureas and selenoureas (in KBr).

Compound	A	B	C	D	E	F	G
<i>N,N</i> -Dimethylthiourea *	1620s	1530s	1352s	{ 1069s 11168m	863s	689s	632m
<i>N,N,S</i> -Trimethylthiouronium iodide	1635vs	1594s	{ 1390m 1424m	1043m	855w	675w	< 610
<i>N,N</i> -Dimethylselenourea *	1612s	1551s	1350s	{ 1048s 11165w	840m	{ 643m 696m	594m
<i>N,N,Se</i> -Trimethylselenouronium iodide	1632vs	1595s	{ 1379m 1410m	1041w	840w	{ 628w 642w	560w,br
<i>N,N</i> -Diethylthiourea *	1632s	1523s	1368vs	{ 1062m 11165w	847m	684w	666m
<i>N,N</i> -Diethyl- <i>S</i> -methylthiouronium iodide	1642vs	1585s	1403m	1082w	837w	700vw	—
<i>N,N</i> -Diethylselenourea	1625s	1532s	1358s	{ 1059m 1170w	826m	683w	603m
<i>N,N</i> -Diethyl- <i>Se</i> -methylselenouronium iodide	1620vs	1565s	1378m	1088m	819w	693w	—
<i>N</i> -Methyl- <i>N</i> -phenylthiourea *	1605s	1480s	1362s	—	809m	689m	not inv.
<i>N,S</i> -Dimethyl- <i>N</i> -phenylthiouronium iodide	1630vs	1551s	1381m	—	822w	690m	not inv.
<i>N,N</i> -Diphenylthiourea	1595s	1432s	1348s	—	820m	692m	not inv.

that the bands are mainly due to C—H vibrations. Nevertheless, the B, C, and D bands could be located by *S*-methylation. The B band disappears (or is weakened considerably) on *S*-methylation and a new band appears at higher frequencies. A complex band near 1100  $\text{cm}^{-1}$  is also affected significantly on *S*-methylation; some peaks are weakened and at least one is shifted toward higher frequencies; in Table 8 this band is considered (perhaps somewhat arbitrarily) to represent the D band. The C band is less characteristic, being only somewhat weakened on *S*-methylation. Below 1000  $\text{cm}^{-1}$  the infrared spectra of corresponding tetrasubstituted thioureas and selenoureas are still very similar and quite different from the spectra of the corresponding ureas.

The G band of tetrasubstituted thioureas is considered to be a band (usually rather weak) near 900  $\text{cm}^{-1}$ . This is a rather high frequency, in accordance with the values found for other tertiary thioamides. In the case of tetramethylthiourea the assignment is unambiguous. There are only very weak absorptions between 870  $\text{cm}^{-1}$  and a medium strong band at 483  $\text{cm}^{-1}$  (478 w in the spectrum of tetramethylselenourea). A medium strong band at 870  $\text{cm}^{-1}$  is shifted less than 5  $\text{cm}^{-1}$  on *S*-methylation or selenation and is ascribed to the methyl groups; a corresponding band is found at 917  $\text{cm}^{-1}$  in the spectrum of tetramethylurea. However, a weak, but sharp band at 956  $\text{cm}^{-1}$  is split into three bands on *S*-methylation, is shifted to 920  $\text{cm}^{-1}$  on selenation and is missing in the spectrum of tetramethylurea; it is therefore considered to be a G band.

Tetraethylthiourea has a medium strong band at 892  $\text{cm}^{-1}$  which is affected by *S*-methylation, complex formation and selenation, and is missing in the spectrum of tetraethylurea. It is similarly considered to be a G band. However, the shifts of the G bands on selenation are rather small for all tetrasubstituted thioureas, so that the C—S vibrations seem to be coupled with C—H vibrations.

## EXPERIMENTAL

### Infrared spectra

The infrared spectra were, in most instances, recorded on a Perkin-Elmer model 21 double beam spectrophotometer with NaCl optics or (for the range below 700  $\text{cm}^{-1}$ ) with KBr optics. In addition, some of the spectra were recorded on a Perkin-Elmer model 125 grating spectrophotometer. Some of the thioureas were only recorded on a Perkin-Elmer "Infracord" spectrophotometer, and in these cases the range below 700  $\text{cm}^{-1}$  was not investigated. In a few cases (indicated by references in the tables) data from the literature have been used. For all solid compounds the KBr disc technique was applied (300 mg of KBr mixed with *ca.* 1 mg of the substance).

Deuteration could usually be performed by heating the compounds gently with heavy water until successive treatment only caused minor changes in the infrared spectra. In some instances it was found necessary to use dioxane or dimethylformamide as solvents, either because of low solubility or to minimize hydrolysis on heating the compound with heavy water.

### Compounds

Most of the compounds used for this investigation are well-known and were available from our stock of chemicals or were prepared by standard methods and recrystallised until pure, as shown by melting points or analyses. The following compounds are either new or require special comment:

Table 8. Infrared absorption bands ( $\text{cm}^{-1}$ ) of tri- and tetrasubstituted thioureas and selenoureas (in KBr).

Compound	B	C	D	F	G
<i>N,N,N'</i> -Trimethylthiourea	{1530vs 1546vs}	{1342s 1369s 1358s 1385s}	{1045m 1062m 1038m 1060m 1032m 1061m 1027m 1062m 1077m 1093m 1073m 1092m}	900m	{643w 660m 630w 655vw 617w 649s}
[Pt(Me <sub>2</sub> N - CS - NHMe) <sub>2</sub> Cl <sub>2</sub> ]	1590vs	1365m		890w	
<i>N,N,N'</i> -Trimethyl- <i>S</i> -benzylthiourenium chloride	1580vs	1365m		886m	
<i>N,N,N'</i> -Trimethylselenourea	{1552vs 1560vs,sh}	{1345s 1380m}		883m	609m
<i>N,N,N'</i> -Triethylthiourea	1534vs	1376s		845m	644m
[Pt(Et <sub>2</sub> N - CS - NH(Et) <sub>2</sub> Cl <sub>2</sub> )]	1570vs	{1378s 1390s 1300s 1320vs}		837w	621w
<i>N,N</i> -Dimethyl- <i>N'</i> -phenylthiourea	1530s	{1396s 1422s}	1140m	766m	not inv.
<i>N,N,S</i> -Trimethyl- <i>N'</i> -phenylthiourenium iodide	{1589vs 1608vs}	{1396s 1350s 1520s 1508s}	1060m	782m	not inv.
<i>N,N'</i> -Dimethyl- <i>N</i> -phenylthiourea	1520s	1350s	1060m	782m	670m
<i>N</i> -Methyl- <i>N,N'</i> -diphenylthiourea	1508s	1340s	1100m	769m	not inv.
<i>N,S</i> -Dimethyl- <i>N,N'</i> -diphenylthiourenium iodide	1625vs	{1372s 1405s}	1040m	—	not inv.
<i>N,N</i> -Dipropyl- <i>N'</i> - $\alpha$ -naphthylthiourea	1530vs	1333s	1139m	{759w 766w}	not inv.
<i>N,N</i> -Diisobutyl- <i>N'</i> -phenylthiourea	1520vs	{1328s 1338s}	1140m	766m	not inv.
<i>N</i> -Ethyl- <i>N,N'</i> -diphenylthiourea	1530m	1328s	1117m	759m	not inv.
<i>N,N</i> -Dipropyl- <i>N'</i> -cyclohexylthiourea	1526vs	1352s	1129m	{717m 747w 744m}	716m
<i>N,N</i> -Dipropyl- <i>N'</i> -cyclohexylselenourea	1523vs	1350s	1129m	—	623m
<i>N,N,N,N'</i> -Tetramethylthiourea	1503s	{1355s 1365s}	1090s	—	956w
Pentamethylthiourenium iodide	1602vs	{1392s 1402s}	1170m	—	{985vw 957vw 935vw}
<i>N,N,N,N'</i> -Tetramethylselenourea	1517m	{1360s 1375s}	1085s	—	920vw
<i>N,N,N,N'</i> -Tetraethylthiourea	1485s	1375s	1082m	—	892m
<i>N,N,N,N'</i> -Tetraethyl- <i>S</i> -methylthiourenium iodide	1560s	1380w	1140w	—	870w
(Et <sub>2</sub> N - CS - NEt <sub>2</sub> )CuCl	1495s	1370m	1138w	—	878m
<i>N,N,N,N'</i> -Tetraethylselenourea	1480m	1380m,sh	1090vs	—	865m
<i>N,N,N,N'</i> -Trimethyl- <i>N'</i> -phenylthiourea	1500vs,sh	1315vs	1095s	—	917w
<i>N,N,N,S</i> -Tetramethyl- <i>N'</i> -phenylthiourenium iodide	{1572vs 1577vs}	1313w	1122m	—	910vw
<i>N,N'</i> -Diethyl- <i>N,N'</i> -diphenylthiourea	1485s	1375vs	1106s	—	862m

*Thioamides*

Most of the thioamides were prepared from the corresponding amides and phosphorus pentasulfide or from nitriles and hydrogen sulfide. The dialkylthioformamides were prepared by the recent method of Walter and Maerten.<sup>39</sup> Some thioamides were prepared from dithioates and amines (*cf.* Holmberg<sup>40</sup>); this is a very convenient method when the carboxymethyl dithioate<sup>31</sup> is in stock:

*N-Methylthioacetamide*,  $\text{CH}_3\text{CSNHCH}_3$ . Carboxymethyl dithioacetate (1.8 g) was dissolved in 1 N NaOH (10 ml) and 1 ml of 40 % aqueous methylamine solution was added. After  $\frac{1}{2}$  h the solution was neutralised and extracted with ether. The ether was removed by evaporation. The residue was recrystallised from ether-light petroleum with addition of activated carbon. Yield: 0.40 g, colourless crystals, m.p. 58°C. (Found: C 40.30; H 7.91. Calc. for  $\text{C}_3\text{H}_7\text{NS}$ : C 40.41; H 7.91). This compound has been prepared earlier from *N*-methylacetamide and phosphorus pentasulfide.<sup>41</sup>

In the same way were prepared: *N,N*-dimethylthioacetamide (m.p. 72–73°C), *N*-methylthiobenzamide (m.p. 79–80°C), *N,N*-dimethylthiobenzamide (m.p. 69–70°C), *N*-methyl-*p*-butoxythiobenzamide (m.p. 60°C), and *N*-isopropyl-*p*-butoxythiobenzamide (m.p. 73°C). With the exception of the two last-mentioned these compounds had been prepared previously by other methods.

*Selenoamides*

Primary selenoamides were obtained from nitriles and hydrogen selenide,<sup>42</sup> *N*-substituted selenoamides (except diisopropylselenoformamide, see below) from the corresponding amides and phosphorus pentaselenide.<sup>15</sup> The following compounds are new:

*N,N*-Diisopropylselenoformamide,  $\text{HCSenPri}_2$ . This compound was prepared by a modification of Walter and Maerten's method<sup>39</sup> for the preparation of dialkylthioformamides. Negative results were obtained when the calculated amount or excess of hydrogen selenide was used, possibly because hydrogen selenide is a stronger acid than hydrogen sulfide.

Through an ice-cooled solution of sodium ethoxide (prepared from 23 g of sodium and 350 ml of ethanol), which was swept free from oxygen by a stream of oxygen-free nitrogen, was passed a slow stream of hydrogen selenide until 64 g (0.8 mole) had been absorbed. To the solution were added 20 g of diisopropylamine and 48 g of chloroform and the solution was refluxed for 48 h while allowing a slow stream of nitrogen to pass through the flask. After cooling, the solution was filtered and the precipitate (NaCl and Se; 90 g) was washed twice with ethanol. The combined solutions were evaporated *in vacuo* and the residue was extracted with chloroform. The filtered chloroform solution was washed with dilute hydrochloric acid and then water. After drying over  $\text{CaCl}_2$ , the solvent was removed *in vacuo* to yield a red oil which partially crystallised on keeping for some days in a refrigerator. Recrystallisation from pentane yielded 5 g of orange-yellow crystals. The unsharp melting point and analyses of this product proved it to be impure and to contain excess selenium. It was, therefore, recrystallised with great loss from water and finally yielded 0.50 g (0.3 %) of pale yellow crystals with m.p. 79–80°C. (Found: C 43.77; H 7.77; N 7.47. Calc. for  $\text{C}_7\text{H}_{15}\text{NSe}$ : C 43.74; H 7.81; N 7.29).

*Diselenomalonamide*,  $\text{CH}_2(\text{CSeNH}_2)_2$ . This compound was prepared from malononitrile and hydrogen selenide, using the directions for the preparation of dithiomalonamide (*cf.* Ref. 30). By recrystallisation of the brown, crude product (8.4 g from 4 g of the nitrile) from methanol-water, made slightly acid with hydrochloric acid, diselenomalonamide was obtained as yellow crystals (yield 36 %) which, however, contained a trace of selenium. An analytically pure sample was obtained by precipitating it from a solution in dimethylformamide by addition of chloroform. M.p. 169–170°C (decomp.). (Found: C 15.75; H 2.83; N 12.38. Calc. for  $\text{C}_3\text{H}_4\text{N}_2\text{Se}_2$ : C 15.80; H 2.66; N 12.28). At room temperature in absence of oxygen, the compound is fairly stable. However, it gradually loses hydrogen selenide and a nitrile band at 2200  $\text{cm}^{-1}$  appears in the infrared spectrum, indicating transformation into cyanoselenoacetamide. The compound is sensitive to oxygen and oxidants but no diselenole derivative seems to be formed.

*N,N*-Dimethylselenobenzamide,  $\text{C}_6\text{H}_5\text{CSeN}(\text{CH}_3)_2$ . A solution of 60 g of *N,N*-dimethylbenzamide was added dropwise to a stirred suspension of 46 g of phosphorus pentaselenide

in 100 ml of dry benzene. The mixture was refluxed for 36 h, cooled, and filtered. Benzene and unreacted dimethylbenzamide were removed by distillation, first at normal pressure and finally at 0.1 mm Hg. The residue (6 g) was dissolved in benzene, and the solution was filtered. On addition of light petroleum and cooling, dimethylselenobenzamide separated as light yellow crystals (4.0 g, 4.7 %). Recrystallisation from benzene-light petroleum gave crystals, m.p. 79–80°C. (Found: C 50.90; H 5.30; N 6.56. Calc. for  $C_8H_{11}NSe$ : C 50.95; H 5.24; N 6.60).

### Thioureas

The following thioureas have not hitherto been described. They were obtained in almost quantitative yields from the appropriate amines (methylamine, butylamine, and dipropylamine) and isothiocyanates in ether and were recrystallised from ethanol-water or benzene-light petroleum.

*N-Methyl-N'-cyclohexylthiourea*,  $C_8H_{16}N_2S$ . M.p. 162–163°C. Found: C 55.60; H 9.52; N 16.23. Calc.: C 55.76; H 9.38; N 16.26.

*N-Butyl-N'-tert-butylthiourea*,  $C_9H_{20}N_2S$ . M.p. 84–85°C. Found: C 57.33; H 10.79; N 14.60. Calc.: C 57.38; H 10.72; N 14.88.

*N-Methyl-N'- $\alpha$ -methylbenzylthiourea*,  $C_{10}H_{14}N_2S$ . M.p. 123–124°C. Found: C 61.90; H 7.37; N 14.44. Calc.: C 61.81; H 7.28; N 14.42.

*N,N-Dipropyl-N'-cyclohexylthiourea*,  $C_{13}H_{26}N_2S$ . M.p. 68–69°C. Found: C 64.33; H 11.02; N 11.60. Calc.: C 64.39; H 10.83; N 11.56.

### Selenoureas

The tetraalkylselenoureas have been described in a separate paper;<sup>56</sup> the other selenoureas were prepared from cyanamides or carbodiimides and hydrogen selenide<sup>43</sup> or from amines and isoselenocyanates.<sup>20,44</sup> In addition to the tetraalkylselenoureas the following selenoureas are new:

*N-Methylselenourea*,  $C_2H_6N_2Se$ . M.p. 154–155°C. Prepared from methyl isoselenocyanate and ammonia in ether (yield 72 %) and recrystallised from benzene-light petroleum. (Found: C 17.53; H 4.47; N 20.00. Calc.: C 17.53; H 4.42; N 20.44).

*N,N'-Dimethylselenourea*,  $C_3H_8N_2Se$ . M.p. 110–111°C. Prepared from methyl isoselenocyanate and methylamine in ether (yield 78 %) and recrystallised from benzene-light petroleum. (Found: C 24.23; H 5.24; N 18.30. Calc.: C 23.85; H 5.35; N 18.55).

*N,N'-Diisopropylselenourea*,  $C_7H_{16}N_2Se$ . M.p. 167.5–168°C. Prepared from *N,N'*-diisopropylcarbodiimide and hydrogen selenide (yield 70 %) and recrystallised from benzene. (Found: C 40.92; H 7.54. Calc.: C 40.58; H 7.78).

*N,N,N'-Trimethylselenourea*,  $C_4H_{10}N_3Se$ . M.p. 105–106°C. Prepared from methyl isoselenocyanate and dimethylamine in ethanol (yield 79 %) and recrystallised from benzene-light petroleum. (Found: C 29.34; H 6.20. Calc.: C 29.09; H 6.12).

*N,N-Dipropyl-N'-cyclohexylselenourea*,  $C_{13}H_{26}N_2Se$ . M.p. 85–86°C. Prepared from dipropylamine and cyclohexyl isoselenocyanate in ethanol (yield 89 %) and recrystallised from ethanol-water. (Found: C 53.60; H 9.12; N 9.75. Calc.: C 53.96; H 9.08; N 9.68).

### S-Alkyl or Se-Alkyl derivatives

The *S*-methyl or *Se*-methyl derivatives can often be obtained analytically pure and in almost quantitative yields by dissolving the thio- or seleno-compound in peroxide-free ether or (preferably) benzene, adding excess methyl iodide to the cooled solution and keeping it in a refrigerator for 1–3 days. The crystalline compound, which separates, is isolated by centrifugation, washed with ether or benzene and dried *in vacuo* over phosphorus pentoxide. Recrystallisation is usually unnecessary and may yield inferior products. The compounds are very hygroscopic and are easily hydrolysed with the formation of methanethiol or methaneselenol. They are sensitive to oxygen and even in absence of air they often decompose rapidly. It has, therefore, not always been possible to determine a well-defined melting point.

The methyl iodide adducts of thioureas, except *N,N'*-dicyclohexylthiourea, tetraethylthiourea, and *N,N,N'*-trimethyl-*N'*-phenylthiourea, and of the following thioamides

were known: thioformamide,<sup>45</sup> dimethylthioformamide,<sup>46</sup> methylthioacetamide,<sup>41</sup> dimethylthioacetamide,<sup>41</sup> thioacetanilide,<sup>47</sup> phenylthioacetamide,<sup>48</sup> thiobenzamide,<sup>49</sup> *N*-methylthiobenzamide,<sup>50</sup> *N,N*-dimethylthiobenzamide,<sup>50</sup> thioformylpiperidine,<sup>46</sup> thio-pivaloylpiperidine,<sup>51</sup> and thiobenzoylpiperidine.<sup>51</sup> *S,N,N*-Trimethylthioacetamidium iodide and *S,N,N*-trimethylthiobenzamidium iodide were originally obtained by addition of methyl iodide to *S*-methyl *N*-methylthioimidates<sup>41,50</sup> but were in this investigation prepared from the *N,N*-dimethylthioamides and methyl iodide. None of the methyl iodide adducts of selenoamides and selenoureas have hitherto been described.

The following preparations are typical:

*S-Methylthioacetamidium iodide*. Thioacetamide (1.0 g) and methyl iodide (1.9 g) were dissolved in peroxide-free ether (20 ml) and the solution was kept for two days in a refrigerator. The crystals were isolated by centrifugation and washed with ether. Yield: 70 %; m.p. 132–133°C. (Found: C 16.57; H 3.75; N 6.48. Calc. for C<sub>3</sub>H<sub>5</sub>NSI: C 16.59; H 3.71; N 6.45).

*N,S-Dimethylthiobutyramidium iodide*. The thioamide (0.5 g) was dissolved in 2 ml of benzene and 2 g of methyl iodide were added. A yellow oil separated which crystallised on shaking and standing in a refrigerator. It was separated by centrifugation, washed with benzene, and dried *in vacuo* over phosphorus pentoxide. M.p. 112–113°C. (Found: I 48.92. Calc. for C<sub>6</sub>H<sub>14</sub>NSI: I 48.97).

In a similar way, the following *S*-methyl derivatives were prepared (melting points are given in parentheses): Methiodides of *N*-methylthioformamide, C<sub>3</sub>H<sub>5</sub>NSI (91–93), *N,N*-dimethylthioacetamide, C<sub>5</sub>H<sub>11</sub>INS (91–92; this compound is mentioned in Ref. 41 but no m.p. was given), *N,N*-dipropylthioformamide, C<sub>8</sub>H<sub>15</sub>INS (98–100), *N,N*-diisopropylthioformamide, C<sub>8</sub>H<sub>15</sub>INS (150–152), thioacetyl piperidine, C<sub>8</sub>H<sub>15</sub>INS (136–137), *N*-methylthiopropionamide, C<sub>6</sub>H<sub>12</sub>INS (127–129), *N*-isopropylthiobutyramide, C<sub>8</sub>H<sub>15</sub>INS (100–102), *N*-methylthiovaleramide, C<sub>7</sub>H<sub>13</sub>INS (113–115), thioformanilide, C<sub>8</sub>H<sub>10</sub>INS (139–140), *N,N*-diisopropylselenoformamide, C<sub>8</sub>H<sub>15</sub>INSe (150–151), *N,N*-dimethylselenoacetamide, C<sub>6</sub>H<sub>12</sub>INSe (102–104), *N,N*-dimethylselenobenzamide, C<sub>10</sub>H<sub>14</sub>INSe (ca. 160, decomp.), *N,N*-dimethylselenourea, C<sub>4</sub>H<sub>11</sub>IN<sub>2</sub>Se (100–101), *N*-ethylselenourea, C<sub>4</sub>H<sub>11</sub>IN<sub>2</sub>Se (76–78), *N,N*-diethylselenourea, C<sub>6</sub>H<sub>13</sub>IN<sub>2</sub>Se (109–112), *N,N'*-diisopropylselenourea, C<sub>8</sub>H<sub>19</sub>IN<sub>2</sub>Se (ca. 130, decomp.), *N,N'*-dicyclohexylthiourea, C<sub>14</sub>H<sub>27</sub>IN<sub>2</sub>S (139–142), *N,N'*-dicyclohexylselenourea, C<sub>14</sub>H<sub>27</sub>IN<sub>2</sub>Se (86–89), tetraethylthiourea, C<sub>10</sub>H<sub>23</sub>IN<sub>2</sub>S (82–84), *N,N,N'*-trimethyl-*N'*-phenylthiourea, C<sub>10</sub>H<sub>17</sub>IN<sub>2</sub>S (113–114). Satisfactory analyses were obtained for all these new compounds.

In a few cases it was necessary to apply other solvents:

*S,S'*-Dimethyldithiomalonamidium bis-iodide. Dithiomalonamide was dissolved in ethanol and excess methyl iodide was added. After 3 h the solution was filtered, benzene was added to initiate precipitation, and the solution kept for 4 days in a refrigerator. The white crystalline precipitate was filtered, washed with benzene, and dried *in vacuo*. M.p. 196–197°C (decomp.). (Found: I 62.25. Calc. for C<sub>5</sub>H<sub>12</sub>I<sub>2</sub>N<sub>2</sub>S<sub>2</sub>: I 60.68).

In a similar manner, but using methylcellosolve as a solvent, *S*-methyldithiobiuretium iodide was prepared from dithiobiuret; the mono-methiodide was formed even with large excess of methyl iodide. M.p. 132–134°C. (Found: I 45.55. Calc. for C<sub>3</sub>H<sub>8</sub>IN<sub>2</sub>S<sub>2</sub>: I 45.76).

*S-Carboxymethyl derivatives*. The thioamides of caprylic and palmitic acid reacted very slowly with methyl iodide but reacted readily with bromoacetic acid in benzene solution at room temperature, giving *S*-carboxymethyl thiooctanamidium bromide, m.p. 134–135°C. (Found: Br 26.53. Calc. for C<sub>10</sub>H<sub>20</sub>BrNO<sub>2</sub>S: Br 26.81) and *S*-carboxymethyl thiohexadecanamidium bromide, m.p. 137–138°C. (Found: Br 19.70. Calc. for C<sub>18</sub>H<sub>36</sub>BrNO<sub>2</sub>S: Br 19.47). The other *S*-carboxymethyl derivatives have been described in earlier publications from this laboratory.<sup>30,31</sup>

The reaction product of selenobenzamide and methyl iodide was very unstable and could not be obtained in the pure state, but here again the reaction with bromoacetic acid proved advantageous. Selenobenzamide (184 mg) was dissolved in hot benzene (10 ml), the solution filtered, and mixed with a solution of bromoacetic acid (150 mg) in benzene (5 ml). There was an immediate separation of colourless crystals which were filtered after cooling of the solution in ice and washed with benzene. Yield: 224 mg (71 %) of *S*-carboxymethyl selenobenzamidium bromide. This substance melts with decomposition at ca. 150°C.

*Metal complexes*

The platinum complexes were prepared according to Kurnakow<sup>52</sup> who described the compounds of thiourea, *N*-methylthiourea, *N*-ethylthiourea, *N,N'*-diethylthiourea, and *N,N,N'*-triethylthiourea. Like the last of the aforementioned compounds, trimethylthiourea formed an orange-coloured, slightly soluble compound of the type  $\text{PtCl}_2\text{L}_2$ . *N,N*-Diisopropylthioformamide formed an ochre complex of the same type.

The copper(I) chloride complexes were prepared by addition of a solution of copper(I) chloride in conc. hydrochloric acid to an aqueous or ethanolic solution of the thioamide, whereby the complex separated as a white (thiourea), yellow (phenylthioacetamide, benzylthiomalonamide), red (thiobenzamide, thiobenzanilide), or red-brown (thionicotinamide) precipitate. With the exception of the already described thiourea complex,<sup>53</sup> they contained  $\text{CuCl}$  and the thioamide in the ratio 1:1, or, for the dithioamide, 2:1; the thionicotinamide complex contained in addition one mole of  $\text{HCl}$ .

The cobalt(II) complexes were prepared by addition of an ethanolic solution of anhydrous cobalt(II) chloride to ethanolic solutions of the dithioamides. On cooling of the solutions dithiooxamide formed a red-brown and *N,N'*-dimethyldithiooxamide a black-green precipitate; from the solution of the dithiomalonamide an olive-green complex was precipitated on addition of light petroleum. All these compounds contained  $\text{CoCl}_2$  and the dithioamide in the ratio 1:1.

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