

## Ultraviolet and Visible Spectroscopic Study on the 1:1 Charge-transfer Complex between *N*-Methyl- $\epsilon$ -thiocaprolactam and Iodine in Nonpolar and Polar Solvents. Infrared and Raman Spectra of the Solid Complex

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Enthalpies and equilibrium constants have been determined for the 1:1 complex of *N*-methyl- $\epsilon$ -thiocaprolactam and iodine in the solvents heptane, carbon tetrachloride, and dichloromethane. The complex is stabilized by transfer from heptane to dichloromethane as evidenced by the increased values of both equilibrium constants and  $-\Delta H^\circ$ . A blue shift of the charge-transfer band occurred in dichloromethane and acetonitrile. A discussion of the vibrational spectra of the donor and the complex is given. The large perturbation of the iodine stretching frequency observed in the Raman spectrum supported the thermodynamic evidence of strong donor-acceptor interaction.

Complex formation between thioureas and iodine has been the subject of extensive studies<sup>1-4</sup> while the information on other types of thioamide- $I_2$  adducts was limited until recently to thioacetamide<sup>1</sup> and the two *N*-methyl derivatives.<sup>4,5</sup> An investigation of the *N,N*-dimethylthioformamide- $I_2$  complex from this laboratory is published,<sup>6</sup> and in the present paper we include the cyclic compound *N*-methyl- $\epsilon$ -thiocaprolactam (MTCL) in the series.

Systematic solvent studies carried out for *N,N*-dimethylthioformamide- $I_2$ <sup>6</sup> showed a marked increase in the equilibrium constant  $K_c$  in the more polar medium in agreement with the observations by Lang<sup>2</sup> for tetramethylthiourea- $I_2$ . Very few of the previously reported types of *CT* complexes are found to have increasing  $K_c$  values in polar solvents. Specifically, these are the strong iodine complexes with amines<sup>7</sup> and triphenylarsine<sup>8</sup> and the trimethylamine-sulfur dioxide adduct.<sup>9</sup> A corresponding increase in the enthalpy of formation  $-\Delta H^\circ$  was conclusive for trimethylamine-sulfur dioxide and indicated for triphenylarsine- $I_2$ , but could not be confirmed for the two thioamides.

MTCL appeared to be well suited for further studies of the solvent effect since the iodine adduct is sufficiently soluble in nonpolar solvents. Although the synthesis has been reported in the literature, spectral data were not available. However,  $\epsilon$ -thiocaprolactam has been studied in the infrared region<sup>10</sup> and also in complex formation with cobalt(II) halides.<sup>11</sup>

Establishment of sulfur as the donor atom in the thioamide- $I_2$  complexes has been based on thermodynamic,<sup>2</sup> NMR<sup>4</sup> and IR studies.<sup>5,6</sup> Conclusive evidence could not be obtained from the infrared spectrum alone because of extensive vibrational coupling and difficulties in the assignment of characteristic thioamide absorption frequencies. However, metal bonding to sulfur has been established by X-ray diffraction in complexes of metal halides with thiourea.<sup>12</sup> In a later survey Jensen *et al.*<sup>13</sup> has pointed out various characteristic infrared bands which behave in the same way on *S*-alkylation and on bonding to metal atoms. Their study presents a valuable aid for location of the donor atom in other thioamide complexes from the infrared spectrum alone.

## EXPERIMENTAL

*Syntheses.*—*MTCL.* The procedure reported by Mecke<sup>10</sup> for the reaction of pyrrolidone with phosphorus pentasulfide was adapted to *N*-methyl- $\epsilon$ -caprolactam in the present work by K. Ruzicka. Lactam (10.8 g) and  $P_4S_{10}$  (10.5 g) were boiled in xylene (20 g) for 2 h with stirring. After evaporation of the solvent under vacuum the remaining yellow oil was distilled at 160–230°C, 1 mm. The product was recrystallized from petroleum ether, sublimed in vacuum and recrystallized once more yielding colourless needles, m.p. 48.5°C. (Found: C 58.98; H 8.93; N 9.69; S 22.62. Calc. for  $C_7H_{13}NS$ : C 58.69; H 9.15; N 9.78; S 22.38.) *N*-Methyl- $\epsilon$ -caprolactam was synthesized from commercial  $\epsilon$ -caprolactam as reported by Benson and Cairns.<sup>14</sup>

*MTCL- $I_3$  and MTCL- $HgCl_2$ .* The solid complexes were prepared in heptane and anhydrous ether, respectively, by mixing solutions containing equivalent amounts of the reactants. (Calc. for  $C_7H_{13}NSI_3$ : I 63.9. Found 63.8. Calc. for  $C_7H_{13}NSHgCl_2$ : Hg 48.4. Found 48.8.)

*Solvents.* Heptane, carbon tetrachloride, dichloromethane and acetonitrile (all Merck *Uvasol* grade) were dried carefully. Resublimed iodine (Merck) was used without purification. Benzene, carbon disulfide, and dichloromethane (all Merck *Uvasol* grade) were used without purification in the infrared and Raman studies.

*Instrumental.* All measurements employed for the calculations of the thermodynamic functions were obtained with a manual Zeiss PMQII ultraviolet-visible spectrophotometer equipped with a thermostatted cell holder. Temperature was maintained constant to about  $\pm 0.2^\circ\text{C}$ , and measured with a YSI telethermometer (42C) utilizing a hypodermic thermistor probe (513) fitted in a narrow boring in the middle of the cell holder. A special double lid was constructed for the cell compartment to permit switching of the cell without removal of probe and connecting cables. Visible and ultraviolet curves were recorded with a Beckman DK-1 spectrophotometer equipped with a thermostatted cell holder. A Perkin-Elmer Model 225 infrared and a Cary 81 Raman spectrophotometer Spectra Physics helium-neon laser were used for recording of the vibrational spectra.

1 cm matched quartz cells were used in all measurements in the ultraviolet and visible regions. The infrared cells were of the conventional type with KBr windows, thickness 0.2–0.5 mm. Silica capillary tubes were used for Raman measurements on solutions.

*Procedure.* The preparation of the solutions has been described previously.<sup>6</sup> In the solvents heptane and carbon tetrachloride  $I_3^-$  was observed in the mixed solutions after 24 h and in dichloromethane after 3–4 h at room temperature. In acetonitrile  $I_3^-$  appeared slowly also in the solutions containing only iodine, but was formed rapidly in the ternary solutions.

*Treatment of data.* The  $K_c$  values were determined as in the previous study.<sup>6</sup> A modified Lang equation was applied to the data obtained from the long wavelengths side of the CT band.  $-\Delta H^\circ$  for the complex formation was calculated from the  $K_c$  values at four temperatures in the interval 14–40°C for heptane and carbon tetrachloride solutions. Temperatures above 33°C were not employed with the lower boiling dichloromethane. The concentration ranges for MTCL were (M): heptane,  $7.7 \times 10^{-5}$  to  $2.2 \times 10^{-3}$ ; carbon tetrachloride,  $7.3 \times 10^{-5}$  to  $5.7 \times 10^{-4}$  and dichloromethane,  $1.1 \times 10^{-5}$  to  $2.2 \times 10^{-4}$ . The iodine concentrations were (M)  $(1.5-3.7) \times 10^{-5}$ ,  $(1.4-6.0) \times 10^{-5}$  and  $(1.3-4.0) \times 10^{-5}$  for the three solvents, respectively. In acetonitrile the donor concentration (M) varied from  $4.8 \times 10^{-6}$  to  $7.2 \times 10^{-5}$  and the iodine concentration was kept constant at  $6.6 \times 10^{-6}$ . 5 cm cells were used with the Beckman spectrophotometer in the latter measurements.

RESULTS AND DISCUSSION

*Thermodynamic characteristics and solvent effects.* MTCL is a stronger donor toward iodine than *N,N*-dimethylthioformamide and *N,N*-dimethylthioacetamide, but weaker than tetramethylthiourea as indicated by the  $K_c$  values in the common solvent carbon tetrachloride. Unfortunately the  $\Delta H^\circ$  values are of less utility in determining the relative complex stability since the variations lie within the experimental uncertainties. The data are listed in Table 1.

Table 1. Equilibrium constants and enthalpy values for thioamide-iodine complexes in carbon tetrachloride.

| Donor   | $K_c^{25}$ (l/mol)     | $-\Delta H^\circ$ (kcal/mol) |
|---|------------------------|------------------------------|
| HC(S)N(CH <sub>3</sub> ) <sub>2</sub>                                 | 1270 ± 60 <sup>a</sup> | 7.8 ± 0.5                    |
| CH <sub>3</sub> C(S)N(CH <sub>3</sub> ) <sub>2</sub>                  | 1190 ± 40 <sup>b</sup> | 9.5 ± 1.5                    |
| (CH <sub>2</sub> ) <sub>5</sub> C(S)NCH <sub>3</sub>                  | 3020 ± 20              | 8.8 ± 0.5                    |
| (CH <sub>3</sub> ) <sub>2</sub> NC(S)N(CH <sub>3</sub> ) <sub>2</sub> | 8000 ± 200             | 10.5 ± 0.5                   |

<sup>a</sup> 20.0°C.

<sup>b</sup> Data from the visible iodine band at 550 nm.

The thermodynamic parameters for MTCL-I<sub>2</sub> in solvents of increasing polarity are contained in Table 2. A marked increase in  $K_c$  is apparent in the polar solvents dichloromethane and acetonitrile and a corresponding

Table 2. Thermodynamic parameters for the *N*-methyl- $\epsilon$ -thiocaprolactam-iodine complex.

| Solvent              | $d^a$ | $K_c^{20}$<br>l/mol | $-\Delta G^\circ_{20}$<br>kcal/mol | $-\Delta H^\circ$<br>kcal/mol | $-\Delta S^\circ$<br>e.u. |
|----------------------|-------|---------------------|------------------------------------|-------------------------------|---------------------------|
| Heptane              | 1.9   | 5200 ± 120          | 4.98 ± 0.01                        | 10.5 ± 0.3                    | 19.1 ± 1.0                |
| Carbon tetrachloride | 2.2   | 3115 ± 30           | 4.68 ± 0.01                        | 8.8 ± 0.5                     | 13.9 ± 1.8                |
| Dichloromethane      | 9.1   | 19400 ± 300         | 5.75 ± 0.01                        | 14.3 ± 0.9                    | 28.7 ± 3.0                |
| Acetonitrile         | 38.8  | 35000 ± 5000        | —                                  | —                             | —                         |

<sup>a</sup> Dielectric constant.

increase in  $-\Delta H^\circ$  occurs in the former solvent. In acetonitrile the formation of  $I_3^-$  interfered too strongly even in very dilute solutions at room temperature. A reversal of the effect appeared in carbon tetrachloride where a distinct lowering of both  $K_c$  and  $-\Delta H^\circ$  was observed.

In weakly interacting donor-acceptor systems a decrease in  $K_c$  and  $-\Delta H^\circ$  with increasing solvent polarity seems to prevail.<sup>2,15</sup> The apparent difference in  $K_c$  has been removed in some cases by treating the system as one involving competing equilibria between one of the reactants and the solvent.<sup>16-18</sup> Also, non-specific solvation effects have been considered to describe the variations in  $K_c$  and  $-\Delta H^\circ$  with solvent.<sup>18,19</sup> In these weakly polar complexes the stronger solvation of the reactants relative to the complex tends to lower the stability in the more polar solvents.

The increase in the  $K_c$  values with solvent polarity observed for some strong complexes indicates a stronger solvation of the polar complex as compared to the uncomplexed donor and acceptor. The stabilization should imply an increase in both  $K_c$  and  $-\Delta H^\circ$  as proposed by Christian *et al.*<sup>9,20</sup> A marked increase in  $-\Delta H^\circ$  between heptane and dichloromethane seems to confirm this prediction in the present work. The failure to observe the same effect in the previous studies on the iodine complexes with tetramethylthiourea and *N,N*-dimethylthioformamide may be due to larger experimental uncertainties and possibly to a smaller variation in  $-\Delta H^\circ$  for the weaker of the two complexes.

While transfer from heptane to carbon tetrachloride produced a lowering of both  $K_c$  and  $-\Delta H^\circ$  in the MTCL and dimethylthioformamide complexes, only a decrease in  $K_c$  was conclusive for tetramethylthiourea. Solvent competition for the donor molecule which was assumed in the dimethylthioformamide- $I_2$  system seems a reasonable explanation also in the present case. Recently McKinney and Popov<sup>21</sup> reported a decrease in both parameters for the highly polar pyridine- $I_2$  complex between the same solvents. A minor increase in  $-\Delta H^\circ$  and a small decrease in  $K_c$  were reported for the latter complex between heptane and dichloromethane, indicating a weaker solvent stabilization as compared to the MTCL- $I_2$  complex.

*The ultraviolet spectrum.* MTCL has two absorptions in the near ultraviolet at 369 nm ( $\epsilon_{\max} = 37$ ) and at 273 nm ( $\epsilon_{\max} = 1.58 \times 10^4$ ) in heptane. The peak at longer wavelength which is blue shifted in the more polar solvents is probably the  $n \rightarrow \pi^*$  transition of the thioamide group while the very small shift of the second band is compatible with a  $\pi \rightarrow \pi^*$  transition. Fig. 1 shows the spectrum in dichloromethane of the donor alone and with increasing concentrations of iodine. The two isosbestic points support the assumption of the formation of only one complex, probably of 1:1 stoichiometry.

A blue shift of the  $\pi \rightarrow \pi^*$  band is indicated by the isosbestic point at 257 nm but the maximum of the new band was not observed. Determination of the band shape and absorption maximum of the *CT* transition have been described previously.<sup>6</sup> Overlap with the blue shifted iodine band or the  $n \rightarrow \pi^*$  absorption<sup>22</sup> may explain the asymmetry appearing as a shoulder or broadening toward longer wavelengths. The half band width was determined from the short wavelength side of the maximum and the oscillator strength calculated according to Lang and Tsubomura.<sup>23</sup> The data are listed in Table 3. A pro-

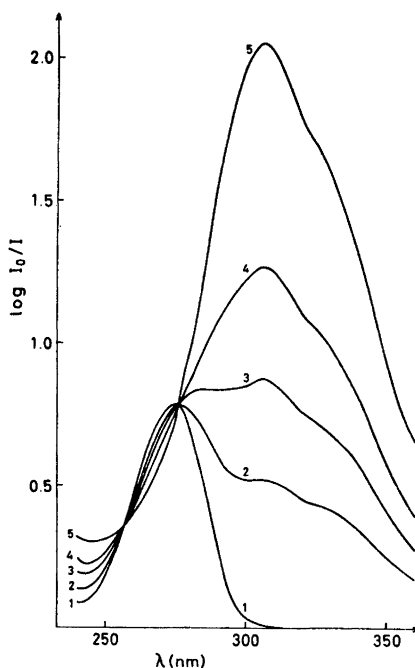


Fig. 1. The ultraviolet spectrum of *N*-methyl- $\epsilon$ -thiocaprolactam ( $4.96 \times 10^{-5}$  M) and iodine in dichloromethane at  $20^\circ$  for a 1 cm cell. The concentrations (M) of iodine are (1) 0, (2)  $3.16 \times 10^{-5}$ , (3)  $6.32 \times 10^{-5}$ , (4)  $1.90 \times 10^{-4}$ , (5) the constructed *CT* band.

nounced blue shift of the *CT* maximum appears in acetonitrile and a small shift is indicated in the less polar solvent dichloromethane. A considerable blue shift was observed in the latter solvent for the tetramethylthiourea- $I_2$  complex while no change occurred for *N,N*-dimethylthioformamide- $I_2$ . The observations indicate some relationship between the strength of the complex and the solvent shift in this case. Variations in the *CT* maximum with solvent polarity has been explained as a result of two opposing effects.<sup>24</sup>

*The blue shifted (BS) iodine band.* This absorption appeared as a separate peak only in heptane. In carbon tetrachloride it occurred as a plateau, and in dichloromethane as a shoulder on the low frequency side of the *CT* band. The absence of this band in acetonitrile may be due to merging with the much

Table 3. The spectral characteristics of the *CT* band of the *N*-methyl- $\epsilon$ -thiocaprolactam-iodine complex in different solvents.

| Solvent              | $\lambda_{\max}$ (nm) | $\epsilon_{\max}$ ( $M^{-1}cm^{-1}$ ) | $\Delta\nu_{\frac{1}{2}}$ ( $cm^{-1}$ ) | <i>f</i> | D (debye) |
|----------------------|-----------------------|---------------------------------------|---|----------|-----------|
| Heptane              | 307.5                 | 35200                                 | 5050                                    | 0.77     | 7.08      |
| Carbon tetrachloride | 310                   | 37900                                 | 5180                                    | 0.85     | 7.47      |
| Dichloromethane      | 306                   | 40900                                 | 6000                                    | 1.06     | 8.32      |
| Acetonitrile         | 293                   | —                                     | —                                       | —        | —         |

stronger *CT* band. At constant iodine and varying donor concentration an isosbestic point occurred in all solvents, supporting the assumption that only one complex is present. The spectral data are listed in Table 4. Because of overlap with the *CT* band the uncertainties in the blue shifted maxima are

Table 4. Spectral characteristics of the blue shifted iodine band of the *N*-methyl- $\epsilon$ -thiocaprolactam- $I_2$  complex in different solvents.

| Solvent              | $\lambda_{I_2}$ (nm) | $\lambda_{BS}$ (nm) | $\lambda_{TBP}$ (nm) | $\epsilon_{max}$ ( $M^{-1} cm^{-1}$ ) |
|----------------------|----------------------|---------------------|----------------------|---------------------------------------|
| Heptane              | 521                  | 431                 | 494                  | 2790                                  |
| Carbon tetrachloride | 516                  | 410–425             | 493                  | —                                     |
| Dichloromethane      | 504                  | ca. 330 sh.         | 478                  | —                                     |
| Acetonitrile         | 461                  | —                   | 463                  | —                                     |

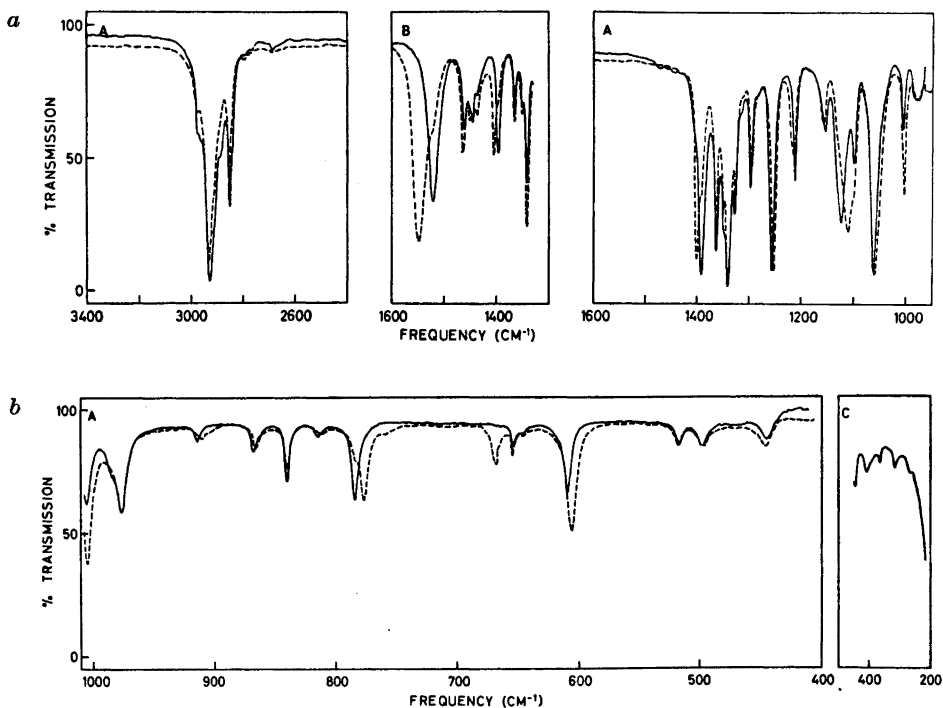


Fig. 2a. The infrared spectrum in the region 3400–950  $cm^{-1}$  of *N*-methyl- $\epsilon$ -thiocaprolactam (solid line) and in a mixture with iodine (dotted line). The concentrations ( $M$ ) of donor and iodine are, respectively, (A) 0.11 and 0.09 in carbon disulfide, cell thickness 0.05 cm and (B) 0.08 and 0.07 in dichloromethane, cell thickness 0.02 cm.

Fig. 2b. The infrared spectrum in the region 1000–400  $cm^{-1}$  of *N*-methyl- $\epsilon$ -thiocaprolactam (solid line) and in a mixture with iodine (dotted line) in carbon disulfide. Concentrations as in Fig. 2a (A). Pure donor as KI pellet (C).

rather large, but a decrease in wavelength with solvent polarity is apparent. In each solvent the shift seems somewhat larger than for dimethylthioformamide- $I_2$ , in accordance with the greater interaction in the former complex.

*Vibrational spectra.* Evidence for bonding to the sulfur atom was obtained from the infrared and Raman spectra. When freshly prepared the solid complex had a yellow colour which turned brown during the infrared scan. A more rapid decomposition took place on exposure to the Raman laser radiation and a fast scan was required. Fig. 2 shows the solution spectrum of the free donor

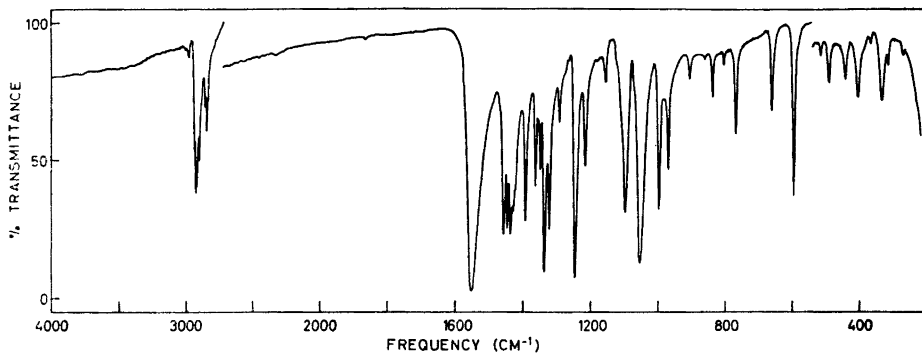


Fig. 3. The infrared spectrum of the solid 1:1 *N*-methyl- $\epsilon$ -thiocaprolactam-iodine complex<sup>a</sup> KI pellet.

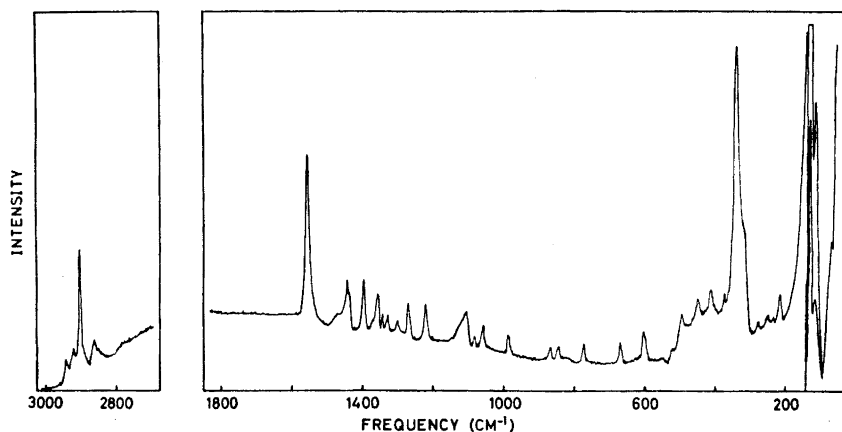


Fig. 4. The Raman spectrum of the solid 1:1 *N*-methyl- $\epsilon$ -thiocaprolactam-iodine complex.

and in a mixture with iodine. The infrared and Raman spectra of the solid 1:1 complex are presented in Figs. 3 and 4. In Table 5 are listed the perturbed infrared donor bands and the data for the 1:1 complex with mercury(II) chloride which are included for comparison.

Table 5. Major changes in the infrared spectrum of *N*-methyl- $\epsilon$ -thiocaprolactam on complex formation (3000–400  $\text{cm}^{-1}$ ).

| MTCL<br>CS <sub>2</sub><br>cm <sup>-1</sup> | MTCL + I <sub>2</sub><br>CS <sub>2</sub><br>cm <sup>-1</sup> | Intensity<br>Change | MTCL · I <sub>2</sub><br>Solid <sup>b</sup><br>cm <sup>-1</sup> | MTCL · HgCl <sub>2</sub><br>Solid <sup>b</sup><br>cm <sup>-1</sup> |
|---|--|---------------------|---|--|
| 2930 s                                      | 2934 s   |                     | 2929 s  | 2935 s   |
| 1521 vs <sup>a</sup>                        | 1549 vs <sup>a</sup>   | Increase            | 1555 vs   | 1565 vs  |
| 1461 s                                      | 1464 s <sup>a</sup>  | Increase            | 1460 s  | 1459 s   |
| 1448 m <sup>a</sup>                         | 1452 m <sup>a</sup>  |                     | 1449 s  | 1445 w   |
| 1437 w <sup>a</sup>                         | 1437 w <sup>a</sup>  | Increase            | 1439 s  | 1440 w   |
|   |  |                     | 1432 w  | 1431 s   |
| 1391 s                                      | 1401 s   |                     | 1395 s  | 1403 s   |
| 1255 s                                      | 1252 s   |                     | 1249 vs   | 1246 s   |
| 1211 m                                      | 1214 m   |                     | 1219 m  | 1220 m   |
| 1154 w                                      | 1157 w   |                     | 1157 w  | 1159 w   |
| 1123 s                                      | 1111 s   | Increase            | 1101 s  | 1105 m   |
| 1005 w                                      | 1004 m   | Increase            | 1001 s  | 1004 m   |
| 840 w                                       | 840 w  | Decrease            | 840 w   | 842 w  |
| 784 w                                       | 777 w  |                     | 771 m   | 771 m  |
| —   | 668 w  | Increase            | 664 m   | 667 w  |
| 609 w                                       | 606 m  | Increase            | 600 s   | 601 m  |
| 444 w                                       | 446 w  | Increase            | 445 w   | 450 w  |

<sup>a</sup> CH<sub>2</sub>Cl<sub>2</sub>. <sup>b</sup> Nujol mull or KI pellet.

In their early study on NH-containing thioamides Mecke *et al.*<sup>10,25</sup> assigned the strong infrared band near 1550  $\text{cm}^{-1}$  to a  $\delta(\text{NH})$  mode while Randall *et al.*<sup>26</sup> and some later workers<sup>27</sup> attributed this band mainly to a  $\nu(\text{CN})$  frequency modified by resonance. The presence of a similar absorption in several fully substituted acyclic thioamides seemed to support the latter assignment.<sup>28</sup> In  $\epsilon$ -thiocaprolactam (TCL) this band was reported at 1545  $\text{cm}^{-1}$  (chloroform)<sup>10</sup> and its counterpart in MTCL is apparently the strong band at 1521  $\text{cm}^{-1}$  (dichloromethane). The shift to higher frequency and the increased intensity in the MTCL complexes are paralleled by the spectral changes in acyclic thioamides on *S*-alkylation<sup>13</sup> and reflect the increased CN double bond character on co-ordination to the sulfur atom. Some contribution from the  $\nu(\text{CN})$  mode may also be responsible for the upward shift of the donor band at 1391  $\text{cm}^{-1}$ .

The strong band at 1123  $\text{cm}^{-1}$  (carbon disulfide) which is shifted to lower frequencies and intensified on complex formation seems closely related to the band reported at 1117  $\text{cm}^{-1}$  (chloroform), in TCL assigned as a localized  $\nu(\text{CS})$  mode. In a more recent work on the TCL-cobalt(II) complexes<sup>11</sup> coupling of this vibration was assumed, which had been verified in the later studies on acyclic thioamides. Partial  $\nu(\text{CS})$  character was attributed also to the vibration at 790  $\text{cm}^{-1}$  in TCL, from the downward shift on bonding to cobalt. In MTCL a pronounced shift to lower frequencies occurred in a donor band at 784  $\text{cm}^{-1}$ , while a smaller shift and strong intensification was apparent at 610  $\text{cm}^{-1}$ . These two bands lie in the region 800–600  $\text{cm}^{-1}$  assigned by the same authors<sup>13</sup> to fairly pure  $\nu(\text{CS})$ , where accordingly the largest frequency decrease should



be expected. However, the larger shift in MTCL was found near  $1100\text{ cm}^{-1}$  and the existence of a fairly pure  $\nu(\text{CS})$  mode seems less probable. These results are consistent with the spectral changes in TCL on selenation,<sup>29</sup> which were published when this paper was in preparation. The authors report only small downward shifts in the region  $800 - 600\text{ cm}^{-1}$  in contrast to the large displacements observed for acyclic thioamides.<sup>13</sup> Also a smaller frequency decrease appeared near  $1115\text{ cm}^{-1}$  in TCL as compared to the 5- and 6-membered ring homologues. Strong vibrational coupling was assumed to take place in the 7-membered ring.

Apparent from Fig. 4 the perturbed infrared bands near  $1550$ ,  $1400$ ,  $1100$ , and  $770\text{ cm}^{-1}$  are easily recognized in the Raman spectrum of the complex. The former band is very prominent in both spectra. In the region below  $300\text{ cm}^{-1}$  there are two strong Raman bands at  $117$  and  $134\text{ cm}^{-1}$ . The former is probably due to  $\text{I}_3^-$  formed on decomposition, while the latter may arise from the iodine stretching frequency in the complex, which appeared at  $145\text{ cm}^{-1}$  in benzene solution. Klæboe<sup>30</sup> reported this band at  $157\text{ cm}^{-1}$  for thiourea- $\text{I}_2$  in accordance with the lower stability reported for this complex.<sup>1</sup>

Friedrich and Person<sup>31</sup> have proposed a semiempirical method for predicting the weight of the dative structure wave function in the complex from the change in the halogen stretching force constant. In strong complexes the bonding between the donor and the halogen also has to be considered which would require, in the present case, knowledge of the S-I stretching frequency. Unfortunately this band escaped observation because of the high background near the exciting line. However, the weight of the dative structure has been determined to 18 % in the stronger tetramethylthiourea- $\text{I}_2$  complex from dipole moment measurements<sup>32</sup> and there is no reason to assume a very different situation in the present case.

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