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# Charge-Transfer Interactions of Iodine with Some Thiones[1]

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Thermodynamic results are reported for the spectrophotometric investigation in carbon tetrachloride of the 1:1 complexes of iodine with the following series of thiones containing the NC═S group: tetraethylthiuram disulfide, $(C_2H_5)_2NC(S)SSC(S)N(C_2H_5)_2$; tetramethylthiuram disulfide, $(CH_3)_2NC(S)SSC(S)N(CH_3)_2$; tetramethylthiuram monosulfide, $(CH_3)_2NC(S)SC(S)N(CH_3)_2$; methyl dimethyldithiocarbamate, $(CH_3)_2NC(S)SCH_3$; and N,N-dimethylthioacetamide, $(CH_3)_2NCS(S)CH_3$.

## Introduction

Of several available electron-donor sites in thiones, it is the carbonyl sulfur which has been found to be the site of interaction, *e.g.*, metal ions,[2-4] hydrogen ion,[5,6] formation of hydrogen bonds,[7] and iodine charge-transfer (CT) complexes. The last includes complexation with thioamides,[7,8] thioureas,[7,8-10] and related thiones.[11] In the present work, the CT studies with iodine are extended mostly to several thiones which contain multiple sulfur sites.

## Experimental Section

**Apparatus.**—Spectral measurements were made with a Cary 14 double-beam, recording spectrophotometer, using 1.00-cm matched quartz cells.

**Procedure.**—The general techniques used to make up solutions and to control the temperature (to ±0.2°) have been described previously.[12] Fresh solutions for each run were made up at 20°, and the concentrations at other temperatures were calculated assuming equal densities of the solutions and the pure solvent (concentrations were less than $10^{-2}$ *M*).

Some solutions were unstable. On long standing the iodine complexes of tetramethylthiuram disulfide and of tetramethylthiuram monosulfide showed a time dependence of the absorbance. In addition, the latter donor in solution showed instability on exposure to light. Storing the solutions in amber bottles for the duration of the run solved the problem. The stability over a temperature range was checked by returning to the initial temperature at the end of the run. The reference cell was not thermostated, but no corrections had to be made because the temperature dependence of the absorption of the solvent was negligible at the wavelengths and temperatures used.

**Reagents.**—Baker "Analyzed" reagent iodine was resublimed from potassium iodide–iodine mixtures and stored in a desiccator in the dark.

Matheson Coleman and Bell (MCB) or Eastman Spectroquality carbon tetrachloride was dried over calcium chloride and distilled immediately before use.

Tetraethylthiuram disulfide (MCB) was recrystallized twice from ethanol; mp 70–71°; lit. mp 70.5°,[13] 72°.[14]

Tetramethylthiuram disulfide (MCB) was recrystallized twice from chloform–ethanol; mp 154–156°; lit. mp 151°,[13] 156°.[14]

Tetramethylthiuram monosulfide (Eastman) was recrystallized twice from ethanol; mp 105–106°; lit. mp 104°,[13] 106°.[14]

Methyl dimethyldithiocarbamate was prepared from dimethylammonium dimethyldithiocarbamate (Eastman) and methyl iodide at 30–40°. The product was extracted several times with ethyl ether and then recrystallized twice from 40–60° petroleum ether; mp 45–47°; lit. mp 45–46°,[15] 47°.[14] *Anal.* Calcd for $C_4H_9NS_2$: C, 35.42; H, 6.71; S, 47.42. Found: C, 35.60; H, 6.60; S, 47.50.

N,N-Dimethylthioacetamide (Eastman) was recrystallized twice from water. *Anal.* Calcd for $C_4H_9NS$: C, 46.55; H, 8.79; S, 31.07. Found: C, 46.59; H, 8.74; S, 31.10.

**Calculations.**—The stability constant, *K*, was determined by a Liptay[16] treatment over six or seven wavelengths, assuming 1:1 interaction and using the well-known quadratic (or full) equation which has been discussed elsewhere.[17,18] The enthalpy and entropy of complex formation were determined from the temperature dependence of the $K\epsilon$ product where $\epsilon$ is the extinction coefficient.

## Results

The donors studied and the thermodynamic results obtained are given in Table I. Distinct CT bands were observed for the iodine complexes with tetraethylthiuram disulfide (Figure 1), tetramethylthiuram disulfide, and methyl dimethyldithiocarbamate. For N,N-dimethylthioacetamide–iodine there is a clear CT maximum, but the band obviously is not a simple one as seen by the shoulder at ~340 mμ (Figure 2). For tetramethylthiuram monosulfide–iodine, there is large overlap between the free-donor band and the CT band, which was resolved by subtracting the absorbances of the equilibrium concentrations of donor and of iodine. The resolved band had a maximum at ~326–328 mμ.

An independent study of the blue-shifted iodine band was made for the tetraethylthiuram disulfide–iodine

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[1] Taken in part from the Ph.D. thesis of A. F. Grand, University of Michigan, Ann Arbor, Mich., 1968.

[2] H. P. Klug, *Acta Cryst.*, **21**, 536 (1966).

[3] (a) M. Bonamico, *et al.*, *ibid.*, **19**, 898 (1965); (b) *ibid.*, **19**, 886 (1965); (c) *ibid.*, **19**, 619 (1965).

[4] (a) E. A. Shugam and L. M. Shkol'nikova, *Soviet Phys. Cryst.*, **3**, 756 (1958); (b) E. A. Shugam and V. M. Levina, *ibid.*, **5**, 239 (1960).

[5] (a) M. J. Janssen, *Spectrochim. Acta*, **17**, 475 (1961); (b) *Rec. Trav. Chim.*, **81**, 650 (1962).

[6] T. Birchall and R. J. Gillespie, *Can. J. Chem.*, **41**, 2642 (1963).

[7] R. J. Niedzilski, R. S. Drago, and R. L. Middaugh, *J. Am. Chem. Soc.*, **86**, 1694 (1964).

[8] R. P. Lang, *ibid.*, **84**, 1185 (1962).

[9] R. P. Lang, *J. Phys. Chem.*, **72**, 2129 (1968).

[10] K. R. Bhaskar, R. K. Gasovi, and C. N. R. Rao, *Trans. Faraday Soc.*, **62**, 29 (1966).

[11] K. R. Bhaskar, S. N. Bhat, A. S. N. Murthy, and C. N. R. Rao, *ibid.*, **62**, 788 (1966).

[12] M. Brandon, M. Tamres, and S. Searles, *J. Am. Chem. Soc.*, **82**, 2129 (1960).

[13] "Dictionary of Organic Compounds," Vol. 1, Oxford University Press, New York, N. Y., 1965.

[14] G. D. Thorn and R. A. Ludwig, "The Dithiocarbamates and Related Compounds," Elsevier Publishing Co., New York, N. Y., 1962.

[15] A. D. Ainley, W. H. Davies, H. Gudgeon, J. C. Harland, and W. A. Sexton, *J. Chem. Soc.*, 147 (1944).

[16] W. Liptay, *Z. Elektrochem.*, **65**, 375 (1961).

[17] M. Tamres, *J. Phys. Chem.*, **65**, 654 (1961).

[18] N. J. Rose and R. S. Drago, *J. Am. Chem. Soc.*, **81**, 6138 (1959).

TABLE I

THIONE–IODINE COMPLEXES IN CARBON TETRACHLORIDE[a]

| Donor | λ, mμ | Temp, °C | $K$,[b,c] l. mol$^{-1}$ | $10^{-4}\epsilon_c$, l. mol$^{-1}$ cm$^{-1}$ | $-\Delta H°$, kcal mol$^{-1}$ | $-\Delta S°$, eu |
|---|---|---|---|---|---|---|
| Tetraethylthiuram disulfide | 356 | 30.0 | 128 ± 31 | 3.90 | 6.38 ± 0.80 | 11.4 ± 2.7 |
| | | 25.0 | 175 ± 21 | 3.47 | | |
| | | 20.0 | 182 ± 34 | 3.90 | | |
| | | 15.4 | 250 ± 21 | 3.63 | | |
| | | 10.0 | 253 ± 67 | 4.10 | | |
| | | | | $\epsilon_{av}$ 3.80 ± 0.22 | | |
| | 460 | 30.0 | 201 ± 4 | 0.265[d] | 6.62 ± 1.11 | 11.3 ± 3.8 |
| | | 20.0 | 281 ± 9 | 0.277[d] | | |
| | | 10.0 | 437 ± 3 | 0.280[d] | | |
| | | | | $\epsilon_{av}$ 0.274 ± 0.008 | | |
| Tetramethylthiuram disulfide | 354 | 30.0 | 111 ± 35 | 3.17 | 7.18 ± 0.62 | 14.4 ± 2.1 |
| | | 20.0 | 152 ± 19 | 3.36 | | |
| | | 15.4 | 194 ± 48 | 3.27 | | |
| | | 10.0 | 249 ± 33 | 3.29 | | |
| | | | | $\epsilon_{av}$ 3.27 ± 0.08 | | |
| Tetramethylthiuram monosulfide | 330 | 30.0 | 287 ± 215 | 2.58 | 7.30 ± 0.66 | 13.0 ± 2.3 |
| | | 20.0 | 433 ± 148 | 2.66 | | |
| | | 15.4 | 443 ± 80 | 3.06 | | |
| | | 10.0 | 647 ± 59 | 2.73 | | |
| | | | | $\epsilon_{av}$ 2.76 ± 0.22 | | |
| Methyl dimethyldithiocarbamate | 347 | 30.0 | 149 ± 26 | 2.46 | 7.53 ± 0.36 | 15.3 ± 1.2 |
| | | 20.0 | 182 ± 28 | 3.03 | | |
| | | 15.4 | 230 ± 36 | 3.03 | | |
| | | 10.0 | 255 ± 58 | 3.45 | | |
| | | | | $\epsilon_{av}$ 2.99 ± 0.44 | | |
| N,N-Dimethylthioacetamide[e] | 310 | 30.0 | 1120 ± 40 | 3.64 | 9.77 ± 0.37 | 18.3 ± 1.3 |
| | | 20.0 | 1990 ± 90 | 3.64 | | |
| | | 10.0 | 3540 ± 270 | 3.70 | | |
| | | 5.0 | 4780 ± 330 | 3.65 | | |
| | | | | $\epsilon_{av}$ 3.66 ± 0.03 | | |

[a] Error limits are for 90% confidence interval. [b] $K$ from quadratic equation. [c] Error limits from linear equation. [d] Uncorrected for the contribution from the overlap with the CT band. [e] Reference 7, study of blue-shifted iodine band in carbon tetrachloride: $K_{25°} = 1190 \pm 40$ l. mol$^{-1}$, $\Delta H° = -9.5 \pm 1.5$ kcal mol$^{-1}$.

complex which was stable at higher concentrations. Free iodine in carbon tetrachloride has a band peak at 516 mμ. The complex gives an isosbestic point, indicative of an equilibrium between only two absorbing species, at 513 mμ. At high donor concentrations, the shifted band has a maximum around 450–460 mμ which overlaps appreciably with the tail of the CT band. Analysis was made at 460 mμ because the free iodine absorption has a negligible temperature dependence at this wavelength and because it is near the band maximum. The contribution from the CT band makes the apparent value of ε of the blue-shifted band high (Table I) and also makes the band maximum appear at a somewhat shorter wavelength.

Mixtures of methyl dimethyldithiocarbamate and iodine also seemed stable at higher concentrations. A semiquantitative study of the blue-shifted iodine band showed a shift comparable to that for tetraethylthiuram disulfide–iodine, with an isosbestic point at 508 mμ.

## Discussion

The thione–iodine complexes interact predominantly in 1:1 ratio over the concentration range studied. This is supported by the observations that (a) good straight lines were obtained from a Scott-type[19] plot which is based on 1:1 complex formation and (b) the Liptay treatment[16] of the data showed no systematic variation in the matrix elements as a function of wavelength.

The one case studied in both the ultraviolet and visible regions, tetraethylthiuram disulfide–iodine, gave agreement in $\Delta H°$, but differed by about 50% in $K$. This may be due in part to different experimental conditions in the two regions. In the ultraviolet, the extinction coefficient of the free donors is several times that of the iodine; hence the complexes were studied using an excess of iodine. At the highest of the iodine concentrations ($5.6 \times 10^{-3}$ $M$) some $I_4$ is formed, which is known to absorb in the ultraviolet region.[20-22] However, in the present study, this does not affect the results. Even assuming the validity of the reported value of 2.28 l./mol for the equilibrium constant at 17° for the formation of $I_4$ in carbon tetrachloride[20] (which seems high),[23] the extent of iodine dimerized is in the range of 1% even in the absence of donor. This is too low a concentration of $I_4$ to contribute to the total absorption near 356 mμ, which is in accord with the obser-

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(19) R. L. Scott, *Rec. Trav. Chim.*, **75**, 787 (1956).

(20) P. A. D. de Maine, *J. Chem. Phys.*, **24**, 1091 (1956).

(21) R. M. Keefer and T. S. Allen, *ibid.*, **25**, 1059 (1956).

(22) M. Tamres, W. K. Duerksen, and J. M. Goodenow, *J. Phys. Chem.*, **72**, 966 (1968).

(23) Keefer and Allen[21] estimated a value of 0.13 l./mol at 25.5°.

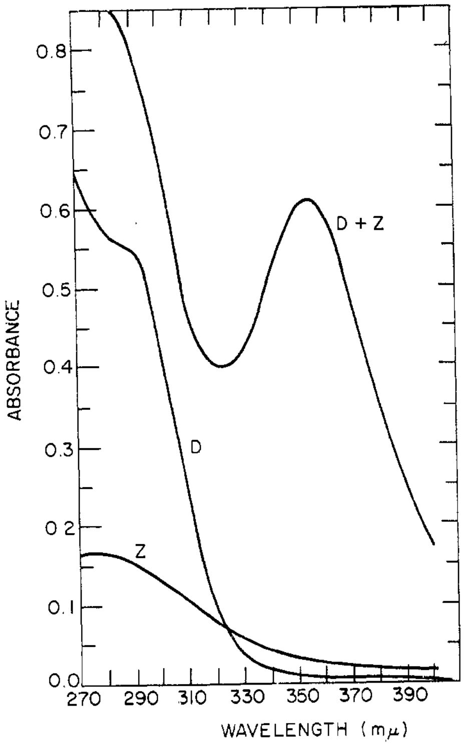

Figure 1.—Ultraviolet absorption spectra of tetraethylthiuram disulfide–iodine in carbon tetrachloride at 20° in 1.00-cm cells: Z = 3.00 × $10^{-3}$ $M$ $I_2$; D = 4.10 × $10^{-5}$ $M$ $(C_2H_5)_2NC(S)SS\text{-}C(S)N(C_2H_5)_2$; D + Z = mixture.

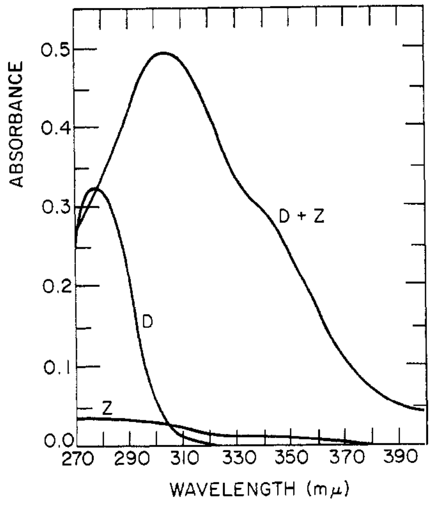

Figure 2.—Ultraviolet absorption spectra of N,N-dimethylthioacetamide–iodine in carbon tetrachloride at 20° in 1.00-cm cells: Z = 8.63 × $10^{-4}$ $M$ $I_2$; D = 2.01 × $10^{-5}$ $M$ $(CH_3)_2NC(S)CH_3$; D + Z = mixture.

vation that a Liptay treatment[16] of the CT data does not indicate the presence of another band.

The donors do not absorb in the visible region; therefore, an excess of tetraethylthiuram disulfide was used to study the blue-shifted band. Since the solvent, in this case carbon tetrachloride, surely is not "inert,"[24,25] competitive reaction with the solvent must be considered. Neglect of solvent competition produces an error[17] in $K$ for the donor–acceptor complex by the factor $1/(1 + K_SS)$, where $K_S$ is the formation constant for donor–solvent and $S$ is the concentration of the solvent. Since $S$ is of the order of 10 $M$, even as small a value for $K_S$ as 0.1 l./mol[26] could alter $K$ by a substantial factor. Using this value of $K_S$ and a $K$ of 250 l./mol for tetraethylthiuram disulfide–iodine and considering the typical concentrations used in this study, the donor at equilibrium is nearly 50% complexed with solvent.

Error analysis of the data showed a much smaller confidence interval for the visible study. In correlation with this, application of the Rose–Drago method[18] gave lines which intersected over a much larger range for the ultraviolet data compared to the rather narrow range for the visible data.

Data for iodine complexes with thiones having various X and Y substituents are presented in Table II. They should be compared only for systems in the same solvent.[27,28] The general similarity in the range of thermodynamic data for the iodine complexes in Table II, in spite of the different X and Y groups, suggests that the donor site is the sulfur in the thiocarbonyl group. Arguments favoring this site have been presented by others,[7-9] the most direct evidence coming from studies on infrared shifts.[10,29]

Unfortunately, the error limits in Table II do not always permit clear distinction in donor strengths, but the data are suggestive of a sequence (in carbon tetrachloride) of tetramethylthiourea (VI) > dimethylthioacetamide (V) > methyl dimethyldithiocarbamate (IV), which parallels reasonably well the donor strengths found by Janssen[5b] toward the hydrogen ion in aqueous sulfuric acid. The donor strengths of several thiones toward iodine also correlate with the relative negative charge (by molecular orbital calculation) on the sulfur in the thiocarbonyl group.[30]

Bhaskar, *et al.*,[11] have compared the results of iodine complexation with carbonyl compounds, X–C(O)–Y, and thiocarbonyl compounds, X–C(S)–Y. In every case, the latter form the stronger adducts, regardless of the nature of the substituents X and Y. However, the data as presented would obscure any attempt to compare the effects of substituents in each of the two series of donors because a range of thermodynamic values is given for several alkyl derivatives of a particular donor and, also, the solvent is not specified.

For iodine complexes with carbonyl donors in carbon

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(24) K. M. C. Davis and M. F. Farmer, *J. Chem. Soc., B*, 28 (1967).

(25) Diethyl sulfide–carbon tetrabromide shows a distinct CT complex: $\lambda_{max}$ 285 mμ, $K_{25°}$ = 0.36 l./mol, $\epsilon_{max}$ 8800 l./mol cm; this laboratory, unpublished results.

(26) This is not an unreasonable value considering the strength of the diethyl sulfide–carbon tetrabromide system.[25] Also, $K$ for mesitylene–carbon tetrachloride has been reported as 0.11 l./mol [R. Anderson and J. M. Prausnitz, *J. Chem. Phys.*, **39**, 1225 (1963)], although this value may be at about the lower limit where a meaningful $K$ can be determined [W. Person, *J. Am. Chem. Soc.*, **87**, 167 (1965)].

(27) R. S. Drago, T. F. Bolles, and R. J. Niedzielski, *ibid.*, **88**, 2717 (1966); (b) W. Partenheimer, T. D. Epley, and R. S. Drago, *ibid.*, **90**, 3886 (1968).

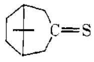
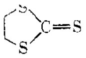
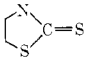
(28) (a) S. D. Christian and J. Grundnes, *Nature*, **214**, 1111 (1967); (b) J. Grundnes and S. D. Christian, *J. Am. Chem. Soc.*, **90**, 2239 (1968).

(29) M. Gerbier and J. Gerbier, *Compt. Rend.*, **263B**, 1057 (1966).

(30) M. J. Janssen, *Rec. Trav. Chim.*, **79**, 1066 (1960).

Table II

Spectrophotometric and Thermodynamic Data for Thione–Iodine Charge-Transfer Complexes

| | Donor | Solvent | $\lambda_{max}$, mμ | Temp, °C | $K$, l./mol | $-\Delta H°$, kcal/mol |
|---|---|---|---|---|---|---|
| I | $(C_2H_5)_2NC(S)SSC(S)N(C_2H_5)_2$ | Carbon tetrachloride[a] | 356 | 20 | 182 ± 34 | 6.38 ± 0.80 |
| II | $(CH_3)_2NC(S)SSC(S)N(CH_3)_2$ | Carbon tetrachloride[a] | 354 | 20 | 152 ± 19 | 7.18 ± 0.62 |
| III | $(CH_3)_2NC(S)SC(S)N(CH_3)_2$ | Carbon tetrachloride[a] | 326–8 | 20 | 433 ± 148 | 7.30 ± 0.66 |
| IV | $(CH_3)_2NC(S)SCH_3$ | Carbon tetrachloride[a] | 347 | 20 | 182 ± 28 | 7.53 ± 0.36 |
| V | $(CH_3)_2NC(S)CH_3$ | Carbon tetrachloride[a] | 306–8 | 20 | 1,990 ± 90 | 9.77 ± 0.37 |
| | | Carbon tetrachloride[b] | ...[g] | 25 | 1,190 ± 40 | 9.5 ± 1.5 |
| VI | $(CH_3)_2NC(S)N(CH_3)_2$ | Carbon tetrachloride[b] | ...[g] | 25 | 8,000 ± 200 | 10.5 ± 0.5 |
| | | Chloroform[c] | 334 | 25 | 13,560 | 9.5 ± 1 |
| | | *n*-Heptane[d] | | 20 | 13,000 ± 1100 | 9.9 ± 1.2 |
| | | Dichloromethane[d] | | 20 | 49,000 ± 5100 | 9.0 ± 1.6 |
| VII | $(C_2H_5)N(H)C(S)(H)N(C_2H_5)$ | Chloroform[c] | 304 | 25 | 15,520 | 14.4 ± 1 |
| VIII | $(i\text{-}C_3H_7)N(H)C(S)(H)N(i\text{-}C_3H_7)$ | Chloroform[c] | 305.5 | 25 | 16,430 | 11.3 ± 1 |
| IX | $(n\text{-}C_4H_9)N(H)C(S)(H)N(n\text{-}C_4H_9)$ | Chloroform[c] | 307.5 | 25 | 40,860 | 18.6 ± 1 |
| X | $H_2NC(S)NH_2$ | Dichloromethane[e] | 298 | 20 | 8,500 | 9.6 ± 1.0 |
| XI | $H_2NC(S)CH_3$ | Dichloromethane[e] | 296 | 17 | 12,000 ± 900 | 8.2 ± 1.8 |
| XII | $(CH_3)N(H)C(S)CH_3$ | Dichloromethane[f] | ~296 | 25 | 540 | 8.4 ± 1 |
| XIII |  | Cyclohexane[f] | ~305[h] | 25 | 95 | 11.0 ± 1 |
| XIV | $(CH_3)N(H)C(S)OCH_3$ | Cyclohexane[f] | ~304 | 27 | 8,120 | 7.3 ± 1 |
| XV | $(i\text{-}C_3H_7)N(H)C(S)OCH_3$ | Cyclohexane[f] | ~304 | 27 | 160 | 7.8 ± 1 |
| XVI |  | Cyclohexane[f] | ...[g] | 25 | 45 | 8.5 ± 1 |
| XVII |  | Chloroform[f] | ~308 | 25 | 1,460 | 10.0 ± 1 |

[a] This research. [b] Reference 7. [c] Reference 10. [d] Reference 9. [e] Reference 8. [f] Reference 11. [g] Data from iodine blue-shifted band; no charge-transfer band maximum reported. [h] Data from iodine blue-shifted band, charge-transfer band maximum reported.

tetrachloride,[31] $\Delta\nu_{CO}$ corresponds to an order of substituent effect on donor strength of $N(CH_3)_2 > CH_3 > SCH_3$. The position of the $OCH_3$ group may be somewhat below $SCH_3$ if $\Delta H°$ or $K$ were to be compared.[31] A similar substituent sequence is observed for $\Delta\nu_{OH}$ in hydrogen bonding of the same carbonyl donors with phenol,[31] except that $OCH_3$ might barely precede $SCH_3$. There is a similarity here with the sequence $N(CH_3)_2 > CH_3 > SCH_3$ for the thione–iodine complexes in Table II. Unfortunately, the data for the iodine complex with O-methyl N-methylthiocarbamate (XIV) cannot be compared directly to determine the relative effect of the $OCH_3$ group because there is one less methyl group on the nitrogen and because cyclohexane is the solvent. For the limited data so far available, at least, there is a consistency in the substituent effects in the carbonyls and the thiocarbonyls, which seems reasonable if these groups are the dominant donor sites in complexation.

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[31] R. L. Middaugh, R. S. Drago, and R. J. Niedzielski, *J. Am. Chem. Soc.*, **86**, 388 (1964).