Chem. Pharm. Bull.
33(1) 225–235 (1985)

N-(2-Thiazolyl)thioureas and Their Copper(II) Chelates. Molecular Species in Solution

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(Received April 10, 1984)

Molecular species of *N*-(2-thiazolyl)thioureas and their Cu(II) chelates present in solution were estimated by analysis of the absorption spectra in the ultraviolet region obtained under various conditions. The *N*-(2-thiazolyl)thioureas studied were 1,1-dimethyl-3-(4-methyl-2-thiazolyl)thiourea (**1a**), 1,1-dimethyl-3-[3,4-dimethyl-2(3*H*)-thiazolylidene]thiourea (**2a**), 1,1-dimethyl-3-(4-methyl-2-thiazolyl)-*S*-methylisothiourea (**3a**), 1,1,3-trimethyl-3-(4-methyl-2-thiazolyl)thiourea (**4a**), 1-monomethyl analogs of **1a**, **2a**, **3a**, and **4a** (**1b**, **2b**, **3b**, and **4b**, respectively), 1-unsubstituted analogs of **1a** and **2a** (**1c** and **2c**, respectively), 1,3-dimethyl-3-(4-methyl-2-thiazolyl)-*S*-methylisothiourea (**5b**), 1-methyl-3-[3,4-dimethyl-2(3*H*)-thiazolylidene]-*S*-methylisothiourea (**6b**), and their derivatives, in which some of the methyl groups were replaced by ethyl groups or the 4-position and/or 5-position of the thiazole moiety were substituted. The thiazole nitrogen atom was more basic than the thiourea nitrogen and sulfur atoms in **1a**, and the predominant species in neutral solvents was the thiazolinylidenethiourea form (II). The predominant species of **1b** and **1c** in neutral media were the thiazolylthiourea (I) form, probably stabilized by an intramolecular hydrogen bond. There was also a difference in the predominant species between **3a** and **3b**. In methanol, **1a**, **1b**, and **1c** formed Cu(II) chelates, which were extracted with chloroform. Cu(II) chelates were also formed from **2a**, **2c**, **3a**, and **3b**, but they were not soluble in chloroform.

Keywords——absorption spectrum; molecular species; Cu(II) chelate; 1,1-dimethyl-3-(4-methyl-2-thiazolyl)thiourea; 1-methyl-3-(4-methyl-2-thiazolyl)thiourea; 3-(4-methyl-2-thiazolyl)-thiourea; 1,1-dimethyl-3-[3,4-dimethyl-2(3*H*)-thiazolylidene]thiourea; 1,1-dimethyl-3-(4-methyl-2-thiazolyl)-*S*-methylisothiourea; 1,1,3-trimethyl-3-(4-methyl-2-thiazolyl)thiourea; 1,3-dimethyl-3-(4-methyl-2-thiazolyl)-*S*-methylisothiourea; 1-methyl-3-[3,4-dimethyl-2(3*H*)-thiazolylidene]-*S*-methylisothiourea

We have shown that derivatives of *N*-(2-thiazolyl)thiourea are a fruitful source of chelating agents which can be used as reagents for spectrophotometric determination of metal ions.[2,3] We synthesized various members of this series of compounds and reported their chemical and physicochemical properties.[2-8] In order to obtain further insight into the characteristics of this series of compounds and their metal chelates, knowledge of the molecular structures of the ligands in solution as well as those of the metal chelates is required.

The absorption spectra of the compounds under various conditions were measured and analyzed in terms of the molecular species present in solution equilibria. The results indicated a difference in predominant species between 1,1-dimethyl-3-(4-methyl-2-thiazolyl)-thiourea (**1a**) and its 1-monomethyl analog (**1b**). The present paper describes the results of the spectral studies on *N*-(2-thiazolyl)thioureas and their metal chelates.

Results and Discussion

Molecular Species

In the molecule of *N*-(2-thiazolyl)thiourea, there are four possible sites for protonation, *i.e.* two nitrogen atoms and a sulfur atom in the thiourea moiety and a nitrogen atom in the thiazole moiety. In this paper, these four sites are denoted as N^1,N^3,S^2, and N^h, as shown in species I of Chart 1. Protonation and deprotonation on these sites give rise to a number of different molecular species for this compound. All possible molecular species of neutral, monoprotonated, and deprotonated states are shown in Chart 1. Roman numerals are used to designate the molecular species. Species I—V are neutral species, whereas VI—IX and X—XIII are monoprotonated and deprotonated species, respectively.

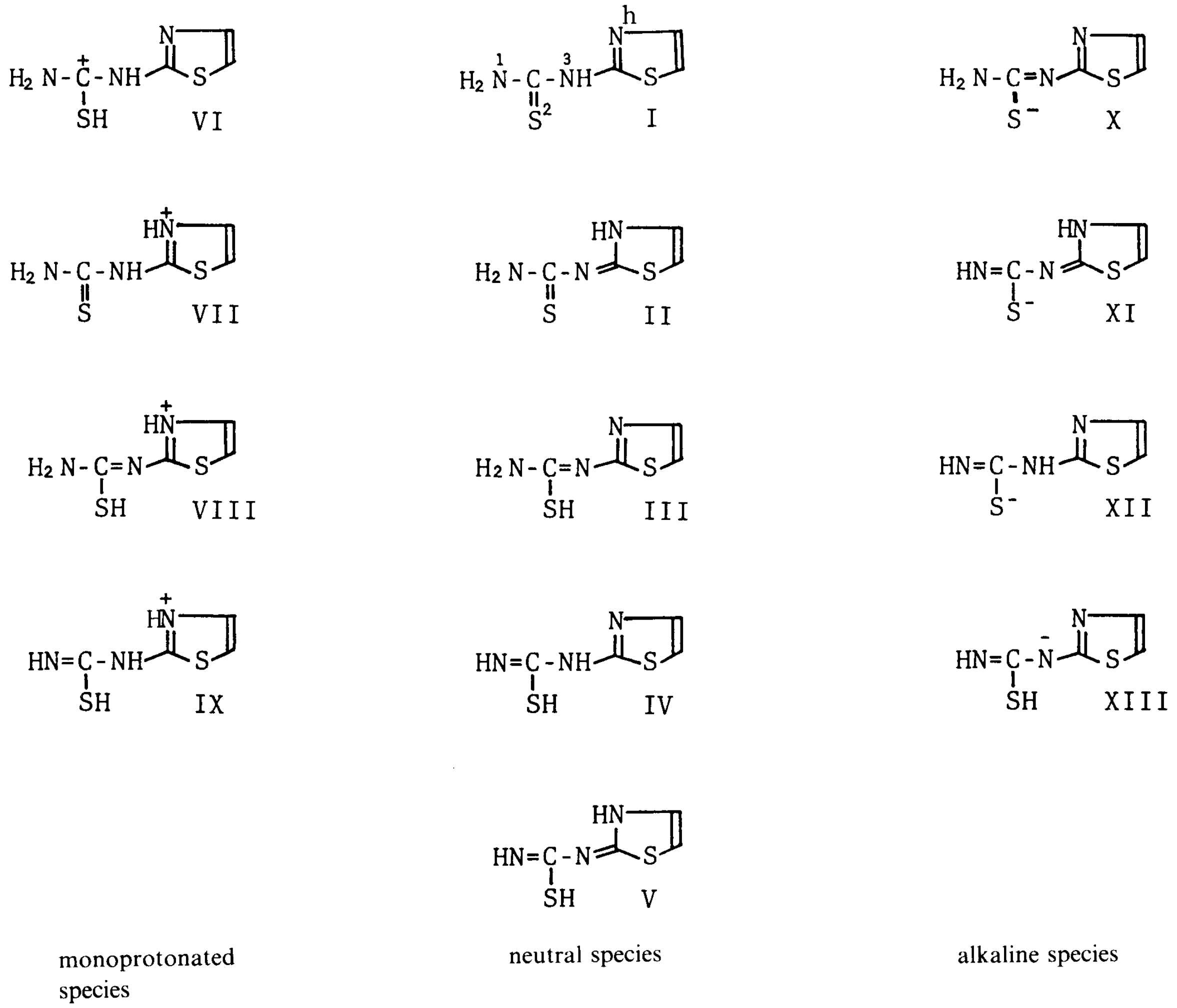


Chart 1

The four protonation sites are also the sites of methylation. We prepared some *N*-(4-methyl-2-thiazolyl)thioureas methylated at these sites. It has been well recognized that the replacement of a dissociable hydrogen by a methyl group does not significantly affect the π–π^* transition bands of an organic molecular species. This principle has been demonstrated by a number of workers[9] in a variety of organic compounds, and we have analyzed the spectra of the thiourea derivatives on this basis. The same Roman numerals are used for the species in which the hydrogen atoms in Chart 1 are replaced by methyl groups, or in some cases by ethyl groups, and also for the species in which the 4- and/or 5-positions of the thiazole moiety are substituted.

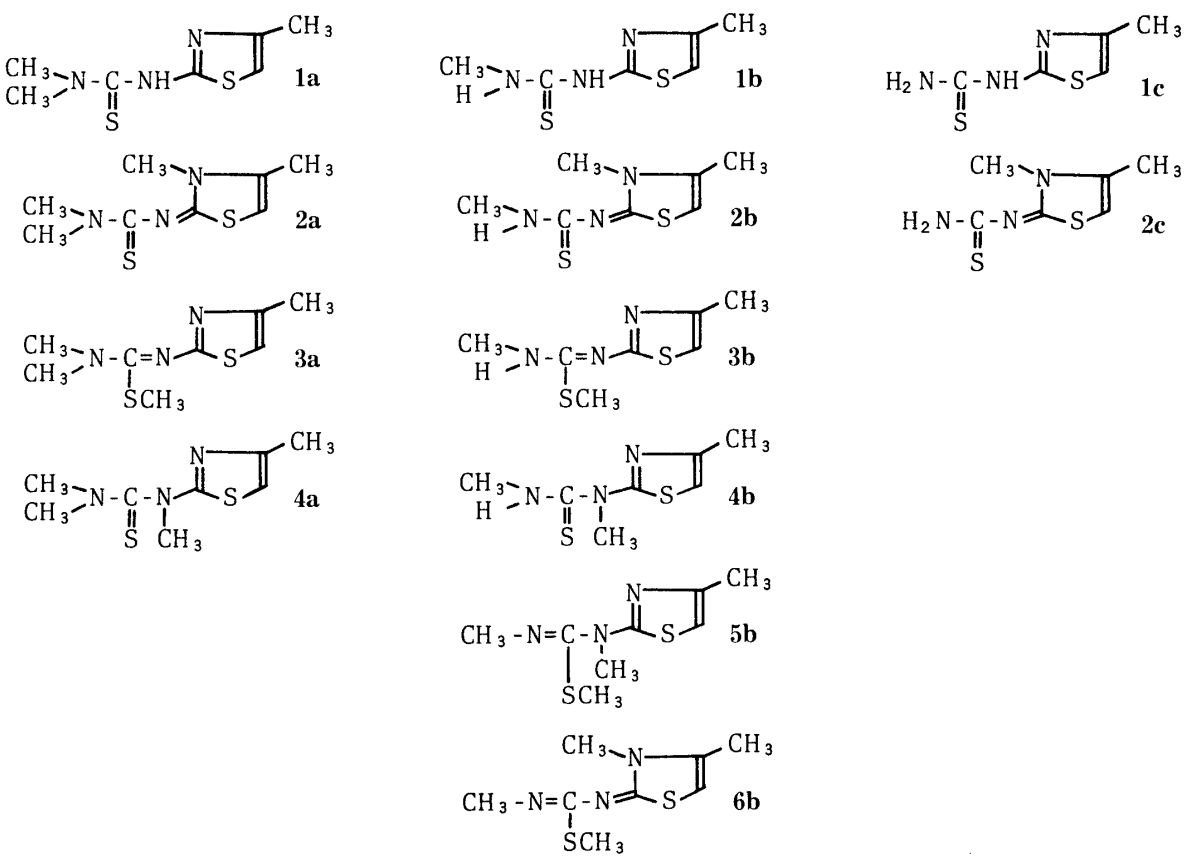


Chart 2

Chart 2 lists the representative compounds used in the spectral study. Arabic numerals accompanied by a letter specify the compounds as shown. Letters a, b, and c indicate N^1-dimethyl, -monomethyl, and -unsubstituted analogs, respectively. An additional arabic numeral is used to indicate compounds in which methyl groups at the four sites are replaced by ethyl groups or the 4- and 5-positions of the thiazole moiety are substituted by other groups. Each species of any specific compound is shown by a Roman numeral with the symbol of the compound as a subscript, such as I_{1a}.

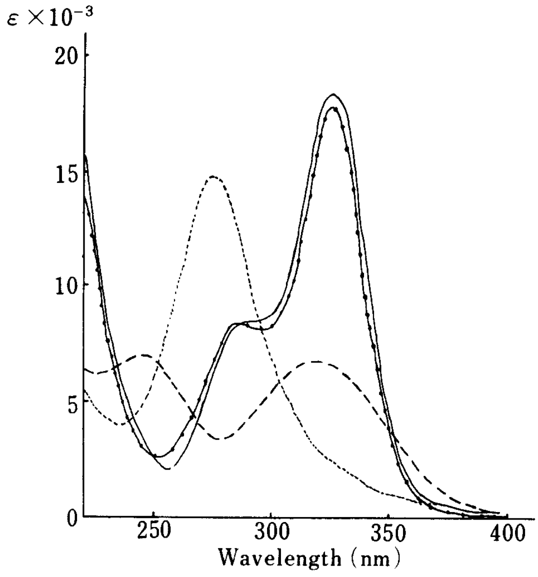
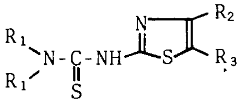
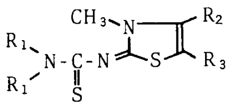
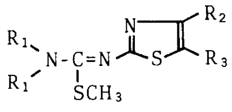


Fig. 1. Absorption Spectra of 1,1-Dimethyl-3-(4-methyl-2-thiazolyl)thiourea (**1a**) and Its Derivatives in Neutral Methanol

—●—, **1a**; ——, **2a**; – – – –, **3a**; ------, **4a**.

TABLE I. Absorption Data and Molecular Species of *N*-(2-Thiazolyl)thioureas

	Compounds				Absorption data [λ_{max} in nm ($\varepsilon \times 10^{-3}$)][a] Molecular species					References
	No.	R_1	R_2	R_3	Neutral methanol	Acidic methanol	Alkaline methanol	$CHCl_3$	Cu(II) chelate in methanol	
	**1a**	CH_3	CH_3	H	326 (17.7) 285 (8.4) II	326sh (5.1) 285 (13.2) II, VII	324 (14.2) 262 (6.6) X	328 (8.7) 293.5 (9.8) 275sh (7.9) II	320 (14.5) 278sh (8.7) XIV	7*b*
	1a$_2$	C_2H_5	CH_3	H	327 (18.7) 290sh (8.7) II	330sh (6.7) 292 (13.1) 230sh (8.3) II, VII	328 (15.8) 266 (6.9) X	335sh (1.3) 291 (14.0) II	323 (16.5) 277sh (9.0) XIV	7*b*
	1a$_3$	C_2H_5	CH_3	CH_3	333 (18.0) 288 (9.1) II	335sh (4.8) 290 (12.6) 228sh (9.8) II, VII	333 (15.3) 266 (7.0) X	333 (12.8) 296 (10.2) 270sh (7.2) II	327 (15.2) 277sh (8.9) XIV	4
	**2a**	CH_3	CH_3	H	326 (18.3) 285sh (8.3) II	326 (16.7) 285sh (8.0) II	326 (18.2) 285sh (8.1) II	328 (17.8) 292sh (9.2) II		7*e*
	2a$_2$	C_2H_5	CH_3	H	327 (19.5) 293sh (9.5) II	327 (18.1) 293 (8.8) II	327 (19.4) 293sh (9.2) II	328 (19.5) 300sh(11.7) II		4
	2a$_3$	C_2H_5	CH_3	CH_3	333 (19.0) 290 (8.5) II	333 (17.4) 290 (8.1) II	333 (18.4) 290 (8.3) II	335 (15.3) 296 (9.2) II		4
	**3a**	CH_3	CH_3	H	319 (6.7) 245 (7.0) III	340 (11.2) 253 (6.7) VIII	317 (6.8) 246 (7.2) III	321 (7.1) 246 (7.4) III	333 (10.3) 250 (8.8) XV	7*e*
	3a$_2$	C_2H_5	CH_3	H	322 (7.7) 249 (7.7) III	342 (12.2) 257 (6.9) VIII	322 (7.7) 249 (7.7) III	324 (7.6) 248 (8.0) III	336 (10.3) 253 (8.6) XV	4
	3a$_3$	C_2H_5	CH_3	CH_3	327 (7.7) 249 (7.5) III	350 (12.1) 258 (6.1) VIII	327 (7.6) 249 (7.5) III	332 (7.4) 248 (7.7) III	346 (12.0) 253 (8.7) XV	4

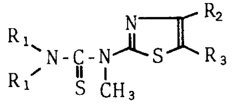
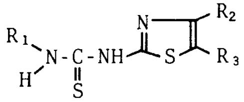
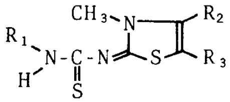
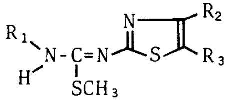
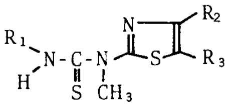
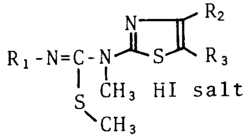
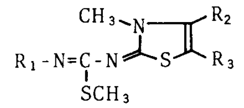
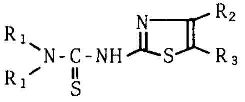
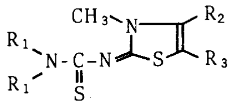
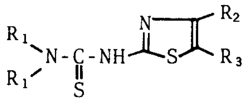
	**4a**	CH_3	CH_3	H	275 (14.8) I	279 (17.4) VII	274 (14.9) I	278 (14.3) I		6
	**1b**	CH_3	CH_3	H	289 (19.3) 253 (8.0) I	289 (12.4) 280sh(12.0) VII	317 (12.3) 260 (5.9) XI	292 (21.1) 257 (8.6) I	303 (14.3) 245sh (6.1) XIV	2, 7*a*
	1b$_2$	C_2H_5	CH_3	H	291 (14.5) 257 (6.4) I	285 (9.5) 222 (7.2) VII	318 (10.3) 260 (5.2) XI	292 (19.7) 259 (8.3) I	303 (14.3) 247 (6.4) XIV	2, 7*a*
	**2b**	CH_3	CH_3	H	323 (17.5) 281 (7.0) II	325 (3.7) 293 (9.8) 276 (10.7) II, VII	323 (17.4) 281 (6.9) II	328 (16.5) 288 (7.3) II	323 (13.7) 245sh (5.8) XVI	7*c*
	2b$_2$	C_2H_5	CH_3	H	324 (17.9) 285 (7.7) II	325 (4.4) 295sh (9.8) 278 (11.1) 222sh (9.8) II, VII	324 (17.9) 285 (7.7) II	328 (16.5) 292 (7.9) II	322 (15.2) 244sh (6.4) XVI	7*c*
	**3b**	CH_3	CH_3	H	308 (15.3) 230sh (6.6) IV or V	325 (18.2) 252 (5.2) IX	308 (15.6) 230sh (6.6) IV or V	312 (17.2) IV or V	320 (14.3) 250sh (6.0) XV	7*e*
	3b$_2$	C_2H_5	CH_3	H	308 (16.6) 230sh (6.7) IV or V	327 (18.7) 253 (5.4) IX	308 (16.6) 230sh (6.7) IV or V	312 (17.6) IV or V	315 (14.7) 235sh (6.9) XV	7*e*
	**4b**	CH_3	CH_3	H	289 (19.6) 257sh (7.4) I	288 (14.8) 226sh (6.6) I	289 (19.2) 257sh (7.4) I	292 (21.4) 259sh (6.6) I		8
	4b$_2$	C_2H_5	CH_3	H	290 (20.3) 260sh (8.3) I	288 (15.5) 260sh (7.5) 227sh (5.7) I	290 (19.5) 260sh (8.0) I	292 (20.6) 259 (6.8) I		7*g*
	**5b**	CH_3	CH_3	H	311 (14.2) 252sh (5.2) IV	326 (18.8) 255sh (9.4) IX	311 (14.2) 252sh (5.2) IV	not soluble		*b)*

Table I. (continued)

	No.	Compounds R$_1$	R$_2$	R$_3$	Absorption data [λ_{max} in nm ($\varepsilon \times 10^{-3}$)][a] Molecular species Neutral methanol	Acidic methanol	Alkaline methanol	CHCl$_3$	Cu(II) chelate in methanol	References
	**6b**	CH$_3$	CH$_3$	H	315 (14.1) 246 (4.5) V	325 (16.1) 250 (5.7) IX	310 (13.8) 239 (5.8) V	313 (14.2) 248 (5.6) V		7*e*
	**1c**	H	CH$_3$	H	292 (19.8) 252 (6.3) I	294 (11.6) 275sh (9.8) VII	315 (12.8) 255 (5.5) 240sh (6.2) XI	298 (22.9) 255 (5.7) I	296 (12.5) 240sh (6.0) XIV	5
	**2c**	H	CH$_3$	H	326 (16.0) 278 (6.9) II	335sh (1.7) 295 (8.4) 273 (9.4) II, VII	326 (15.8) 278 (6.8) II	332 (15.9) 281 (6.8) II	332 (13.6) 290sh (8.0) 240sh (8.1) XVI	5

a) sh indicates shoulder. *b*) Present paper.

Table II. Absorption Data for 1,1-Dialkyl-3-(2-Thiazolyl)thioureas



No.	R_1	R_2	R_3	Absorption data UV λ_{max} nm ($\varepsilon \times 10^{-3}$)[a] Neutral methanol	Absorption data UV λ_{max} nm ($\varepsilon \times 10^{-3}$)[a] $CHCl_3$	References
1a$_4$	CH_3	-Ph	H	328 (1.1) 290sh (14.5) 270 (17.5) 230 (2.4)	335sh (4.0) 267 (22.2)	3
1a$_5$	CH_3	-Ph-CH_3	H	330 (12.3) 274 (18.5) 238 (23.0)	335 (5.8) 268 (24.9)	7*f*
1a$_6$	CH_3	-Ph-Cl	H	322sh (8.3) 273 (18.6) 241 (21.6)	270 (23.5)	7*f*
1a$_7$	CH_3	-Ph-Br	H	323sh (9.9) 274 (21.9) 243 (24.7)	271 (28.9)	7*f*
1a$_8$	CH_3	-Ph-NO_2 (*p*)	H	336 (14.2) 285sh (14.2) 263 (17.2) 232 (20.5)	350 (14.5) 290sh (14.2) 268 (18.7)	7*f*
1a$_9$	CH_3	-Ph-NO_2 (*m*)	H	330 (4.7) 290sh (15.7) 266 (24.3) 234 (21.7)	330sh (1.6) 293sh (15.7) 267 (28.7)	[b]
1a$_{10}$	CH_3	-Ph-NO_2 (*o*)	H	321 (7.5) 290sh (11.8) 263 (19.1) 214 (27.0)	330sh (2.5) 293sh (10.7) 264 (22.6)	[b]
1a$_{11}$	CH_3	-Ph-NO_2 (*p*)	NO_2	470sh (2.6) 367 (8.6) 293sh (19.1) 265 (20.3)	363 (9.8) 292sh (20.2) 268 (22.4)	3
1a$_{12}$	CH_3	-Ph-NO_2 (*m*)	NO_2	465sh (2.1) 378 (7.8) 300sh (9.3) 255 (22.4)	363 (10.4) 258 (32.2)	[b]
1a$_{13}$	CH_3	-Ph-NO_2 (*o*)	NO_2	470sh (2.5) 377 (9.7) 295sh (10.6) 248 (20.9)	360 (11.1) 251 (25.8)	[b]
1a$_{14}$	CH_3	-Ph-CH_3 (*p*) $\diagdown NO_2$	NO_2	450 (2.9) 380 (3.0) 300sh (5.8) 255 (9.7)	365 (11.3) 310sh (10.1) 273 (26.4)	[b]
1a$_{15}$	CH_3	CH_3	NO_2	443 (11.3) 388 (11.6) 292 (6.9)	362 (12.8) 300 (6.0)	3
1a$_{16}$	C_2H_5	CH_3	NO_2	460sh (3.0) 388 (13.0) 293 (7.6) 265 (8.2)	363 (11.8) 299 (5.6)	3

a) sh indicates shoulder. *b*) Presented paper.

Spectral Analysis

Absorption spectra in the ultraviolet (UV) region were obtained for neutral, acidic, and alkaline methanol solutions of the *N*-(2-thiazolyl)thioureas. The acidic and alkaline solutions contained 5×10^{-3} M perchloric acid and potassium hydroxide, respectively, unless otherwise noted.

Absorption spectra of **1a**, **2a**, **3a**, and **4a** in neutral methanol solution are shown in Fig. 1. For N^1-dimethyl derivatives, species, IV, V, IX, XI, XII, and XIII do not exist. The species protonated at N^1 are expected to have the same spectral characteristics as, and to be indistinguishable from, the unprotonated ones. For **2a**—**4a**, spectra in alkaline solutions were the same as those in neutral solutions. Since these compounds have no dissociable hydrogen, the same species should be present in both neutral and alkaline solutions, *i.e.* II_{2a}, III_{3a}, and I_{4a}. The spectrum of **2a** in acidic solution was the same as those in neutral and alkaline solutions, indicating that further protonation on S^2 and N^3 did not occur under the conditions used. Acidification of a methanol solution of **4a** brought about a slight bathochromic and hyperchromic shift of the band at 275 nm. A similar shift was previously reported for the band of **3a**.[4] These shifts are ascribed to the protonation of N^h, *i.e.* formation of VIII_{3a} and VII_{4a}. A red shift of π-bands accompanying protonation of an aromatic nitrogen atom has been demonstrated in a variety of compounds.[9]

It is clear from the spectra that the predominant species of **1a** in neutral methanol is the thiazolinylidenethiourea species (II) and not the thiazolylthiourea species (I). Spectra in other solvents such as 2-propanol and chloroform indicated the same predominant species[7] (Table I). The spectrum in acidic methanol had an absorption band at 285 nm, which was ascribed to VII_{1a}. Under alkaline conditions, a band was observed at 324 nm and was assigned to X_{1a}.

The spectra of **2b** and **4b** in neutral methanol were quite similar to those of **2a** and **4a**, respectively. These results indicate that **2b** and **4b** are in forms II and I, respectively. In contrast to **1a**, **1b** should be present predominantly in form I, since the spectrum of **1b** was almost superimposable on that of **4b** but was significantly different from those of **1a** and **2b**. Similarly, the spectra of **1c** and **2c** indicated that the predominant form of **1c** is the thiazolylthiourea species (I). Compound **5b** was obtained as a hydroiodide and the spectrum of this salt in methanol may be that of IX_{5b}. Addition of an equimolar amount of alkali to the solution gave a spectrum similar to that of **6b**. The spectra of **3b**, **5b**, and **6b** were quite similar in both acidic and neutral states. Under neutral conditions, **5b** and **6b** should be present as species IV and V, respectively. The facts suggest that **3b** is present as IV or V or an equilibrium mixture of these species under neutral conditions. This is in contrast to **3a**, which exists as species III. We reported that the pyrolysis of **3a** gave **2a**, whereas that of **3b** did not give **2b** under similar conditions.[4] These results may now be explained in terms of the difference in the molecular species of **3a** and **3b**.

From the spectral analysis described above, we concluded the thiazole *N* (N^h) is more basic than the thiourea *N* (N^3) or *S*. Therefore thiazolinylidenethiourea II_{1a} and thiazolinylideneisothiourea V_{3b} are the predominant species. The thiazolylthiourea species of **1b** and **1c** (I_{1b}, I_{1c}) may be stabilized by an intramolecular hydrogen bond (Chart 3), which is supported by an X-ray crystallographic study.[10]

Table I lists the spectral data and the assignments of bands made along the lines described above. Table II summarizes the spectral data for derivatives of **1a** with substituents at the 4-position and 5-position of thiazole, some of which were reported previously. When the methyl group at the 4-position of thiazole of **1a** was replaced by a phenyl or *p*-substituted phenyl group, the band at 326 nm assigned to II showed only a slight red shift. This indicates that the thiazolyl and the phenyl groups are only poorly conjugated. However, the absorbances of the bands due to species II decreased and those due to species I increased in the 4-aryl derivatives. These findings indicate that these derivatives were present as an equilibrium mixture of I and II in neutral methanol and in chloroform. Species I was predominant in chloroform solutions of the *p*-chlorophenyl and *p*-bromophenyl derivatives. The basicity of N^h was decreased in these compounds due to the electron-attracting property of the 4-substituents and hence the thiazolylthiourea (I) species may be stabilized, especially in nonpolar solvents. The 4-*p*-nitrophenyl derivative was in form II. The data in Table II also indicate that the introduction of a nitro group at the 5-position brought about a considerable red shift of the bands of species II.

Copper(II) Chelates

In the previous studies,[2,3] metal chelation of thiazolylthioureas was examined by measuring the coloration of chloroform extracts from aqueous or methanolic solutions of a ligand and a metal ion. By this method, **1a**, **1b**, and **1c** were proved to form 1 : 2 metal chelates with Cu(II) and Pd(II), while other compounds listed in Chart 2 did not form chelates. A few Pd(II) chelates of **1a** derivatives were studied by means of X-ray crystallography. The results, which will be reported shortly, showed that the thiazolylthioureas chelated Pd(II) through S^2 and N^h, supporting the structure proposed previously.[2,3]

An equimolar or excess amount of Cu(II) was added to a methanol solution of each of the compounds listed in Table I and the spectra in the UV region were recorded. The results are included in Table I. The spectra of the Cu(II) chelates of **1a**, **1b**, and **1c** were similar to that of species III and can be ascribed to the chelate species XIV shown in Chart 3. Addition of Cu(II) to **3a** and **3b** caused a considerable spectral change. Since the ligands did not form metal chelates extractable by chloroform, the spectral changes should be ascribed to the

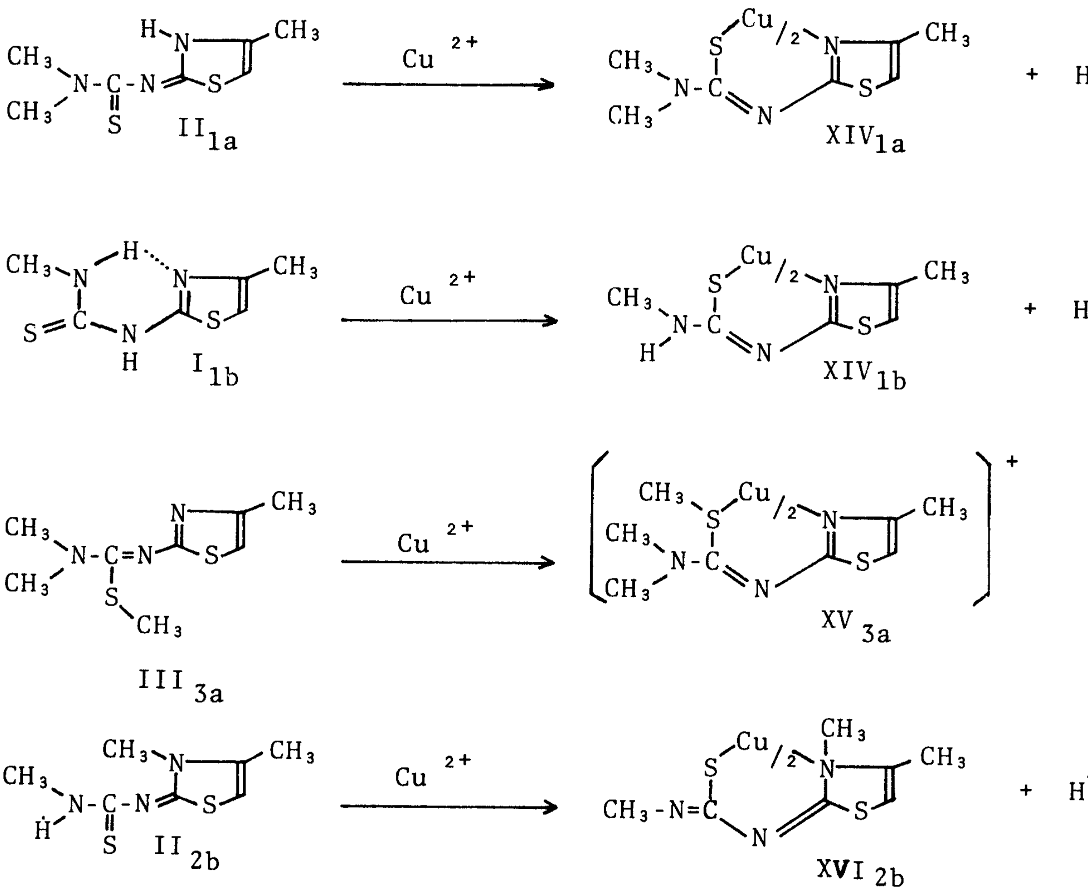


Chart 3

formation of charged metal chelates. The spectra were similar to that of species VIII and the most probable structure of the chelates is XV.

In the spectra of **2b** and **2c**, there were slight but distinct differences between in the presence and in the absence of Cu(II). No such difference was observed in the spectrum of **2a**. In the presence of Cu(II), the absorbance of the π–π^* bands of **2b** and **2c** at the longest wavelength was decreased, and the spectra became similar to that of V$_{6b}$. The spectral change was ascribed to the formation of Cu(II) chelates as XVI. The present study shows that **2b**, **2c**, **3a**, **3b**, and related compounds form Cu(II) chelates in methanol, though their stabilities may not be as large as those of **1a**, **1b**, and **1c**.

No appreciable spectral change was observed in **4a**, **4b**, **5b** and **6b** on the addition of Cu(II).

Experimental

The electronic absorption spectra were recorded at room temperature on a Shimadzu UV-200s double-beam spectrometer. Solutions for the spectral studies were prepared immediately before measurements by dissolving the compound under investigation in a spectrograde solvent followed by appropriate dilution. The acidic and alkaline solutions were obtained by adding standard methanol solutions of $HClO_4$ or KOH. The concentration of the acid or alkali was 5×10^{-3} M unless otherwise noted. Methanol solutions of Cu(II) chelates were obtained by adding standard methanol solutions of Cu(II) perchlorate.

Most of the *N*-(2-thiazolyl)thioureas used in the present study were prepared as described in the references cited in Tables I and II. Compounds **5b**, **1a**$_9$, **1a**$_{10}$, **1a**$_{12}$, **1a**$_{13}$, and **1a**$_{14}$ were not reported in the previous papers.

1,3-Dimethyl-3-(4-methyl-2-thiazolyl)-*S*-methylisothiourea (5b) Hydroiodide——Methyl iodide (1 g) was added to an EtOH solution of **4b** (0.5 g/6 ml). The mixture was heated at 58 °C for 3.5 h and left overnight at room temperature. The white precipitate was filtered off and recrystallized from EtOH. It was positive in the Beilstein test. mp 210—211 °C. Yield, 100 mg. *Anal.* Calcd for $C_8H_{14}IN_3S_2$: C, 28.07; H, 4.12; N, 12.28. Found: C, 28.03; H, 4.17; N, 11.88. Mass spectra (MS) *m/e*: 215 (M^+ − HI), 168 (M^+ − [HI + CH_3S]), 128 (2-methylamino-4-methylthiazole$^+$).

1,1-Dimethyl-3-(4-*m*-nitrophenyl-2-thiazolyl)thiourea (**1a**$_9$) and 1,1-dimethyl-3-(4-*o*-nitrophenyl-2-thiazolyl)thiourea (**1a**$_{10}$) were prepared by a method similar to that used for the *p*-nitrophenyl analog (**1a**$_8$).[7f]

1a$_9$ was recrystallized from a dioxane–EtOH–water mixture. mp 154 °C. *Anal.* Calcd for $C_{12}H_{12}N_4O_2S_2$: C, 46.74; H, 3.92; N, 18.17. Found: C, 46.93; H, 3.94; N, 17.61. MS *m/e*: 308 (M^+), 263 (M^+ − $(CH_3)_2NH$).

1a$_{10}$ was recrystallized from dioxane. mp 179—180 °C. *Anal.* Calcd for $C_{12}H_{12}N_4O_2S_2$: C, 46.74; H, 3.92; N, 18.17. Found: C, 46.61; H, 3.94; N, 17.59. MS *m/e*: 308 (M^+).

1,1-Dimethyl-3-(5-nitro-4-*m*-nitrophenyl-2-thiazolyl)thiourea (**1a**$_{12}$), 1,1-dimethyl-3-(5-nitro-4-*o*-nitrophenyl-2-thiazolyl)thiourea (**1a**$_{13}$), and 1,1-dimethyl-3-[5-nitro-4-(4-methyl-3-nitrophenyl)-2-thiazolyl]thiourea (**1a**$_{14}$) were prepared by a method similar to that used for the *p*-nitrophenyl analog (**1a**$_{11}$).[3]

1a$_{12}$ was recrystallized from DMSO–EtOH. mp 235 °C. *Anal.* Calcd for $C_{12}H_{11}N_5O_4S_2$: C, 40.78; H, 3.14; N, 19.82. Found: C, 40.73; H, 3.27; N, 19.64. MS *m/e*: 353 (M^+), 308 (M^+ − $(CH_3)_2NH$), 88 ($(CH_3)_2NCS^+$).

1a$_{13}$ was recrystallized from acetone–water. mp 226 °C. *Anal.* Calcd for $C_{12}H_{11}N_5O_4S_2$: C, 40.78; H, 3.14; N, 19.82. Found: C, 41.10; H, 3.31; N, 19.55. MS *m/e*: 353 (M^+).

1a$_{14}$ was recrystallized from $CHCl_3$–DMSO. mp 244 °C. *Anal.* Calcd for $C_{13}H_{13}N_5O_4S_2$: C, 42.50; H, 3.57; N, 19.06; S, 17.45. Found: C, 43.40; H, 3.66; N, 19.06; S, 17.44. MS *m/e*: 367 (M^+), 322 (M^+ − $(CH_3)_2NH$), 88 ($(CH_3)_2NCS^+$).

Acknowledgement The authors wish to express their appreciation to Miss Tomoko Okada and Miss Noriko Ogihara for invaluable assistance during the present work. Thanks are due to the members of the Department of Physical Chemistry, the Central Research Laboratories, Sankyo Co., Ltd., for elemental analysis.

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