

Synthesis and properties of some formylferrocene thiosemicarbazones¹

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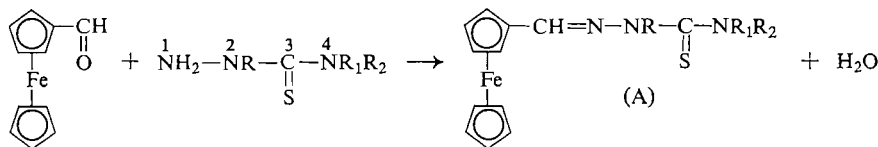
Twelve new substituted thiosemicarbazones have been prepared from formylferrocene and 2- and 4-monosubstituted and 4,4-disubstituted thiosemicarbazides. The infrared spectra of these compounds are discussed in some detail. Copper complexes of three of them were synthesized and their structures established. They were found to be strongly paramagnetic. The electronic absorption spectra of the thiosemicarbazones and the copper complexes are reported.

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Introduction

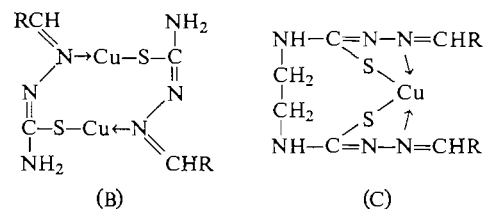
There have been numerous publications, in recent years, dealing with the chemistry of ferrocene and with the many derivatives which can be prepared from it (e.g. ref. 1). Considerable interest has been shown in the reactions of formylferrocene. It is easy to synthesize and many additional ferrocenes may be derived from it. Both the semicarbazone (1) and the simple thiosemicarbazone (2) of formylferrocene have been synthesized.

In the present work, the preparation and some properties of formylferrocene thiosemicarbazones are described. The syntheses involved the reaction of formylferrocene with thiosemicarbazide and substituted thiosemicarbazides. This method produced a set of compounds which have not been reported previously, except for formylferrocene thiosemicarbazone (A; R = R₁ = R₂ = H), mentioned by Boichard *et al.* (2). The structure of A was deduced from infrared spectra and from analytical data.



Some benzoylferrocenes have been shown (3) to retard the actinic degradation of polymer films and the photodecomposition of ferrocenes in hydroxylic (4) and alkyl halide (5) solvents has been reported. However, very little use has been made of particular ferrocene derivatives as protective ultraviolet absorbers in spite of the fact that ferrocenes absorb strongly in the important, near-ultraviolet region. The electronic absorption spectra of the new compounds reported here were measured in order to indicate the potential effectiveness of them as photoprotective agents.

It is known that copper will form 1:1 complexes (B) with thiosemicarbazones (6) and a different type of 1:1 complex (C) with dithiosemicarbazones (7). Copper complexes of three of the ferrocene thiosemicarbazones reported here



were prepared using cupric acetate. These are interesting organometallic - metal - chelate compounds, somewhat analogous to the copper complexes of diacylferrocenes reported previously (8).

Experimental

Methods and Materials

Formylferrocene was prepared by the method of Broadhead and co-workers (9), and was purified by recrystallizing from aqueous ethanol.

2-Methylthiosemicarbazide was prepared by the method of Greer and Smith (10) and was recrystallized from water.

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4,4-Dimethylthiosemicarbazide was prepared by the method of Jensen (11) and was purified by recrystallizing from water.

Thiosemicarbazide was purchased from commercial sources and purified by recrystallizing from water.

All the alkyl and aryl isothiocyanates were obtained from commercial sources and were used as received.

A series of 4-substituted thiosemicarbazides was synthesized by the following method. Hydrazine hydrate (0.022 mole, 99%) in ethanol (25 ml) was added dropwise to a solution of the required isothiocyanate (0.022 mole) in diethyl ether (50 ml). The resulting mixture was stirred for 1 h with gentle heating and reduced to $\frac{1}{3}$ of the original volume. The precipitate, which formed when the mixture was cooled, was removed by filtration, washed with cold ether, dried, and recrystallized. The compounds listed below were made by this method, and were purified by recrystallization from aqueous ethanol unless otherwise stated.

4(1-Naphthyl)thiosemicarbazide, m.p. 139.5 °C (lit. value (12) 139 °C).

4-Phenethylthiosemicarbazide, m.p. 119 °C (no lit. value).

4(*m*-Nitrophenyl)thiosemicarbazide, m.p. 175.5 °C (lit. value (13) 175 °C).

4(*p*-Nitrophenyl)thiosemicarbazide, m.p. 191 °C (lit. value (14) 190 °C).

4-Phenylthiosemicarbazide, m.p. 141 °C (lit. value (15) 141 °C); recrystallized from water.

4-Methylthiosemicarbazide, m.p. 136 °C (lit. value (16) 137 °C).

4-Ethylthiosemicarbazide, m.p. 84 °C (lit. value (16) 84 °C).

4-Heptylthiosemicarbazide, m.p. 54 °C (lit. value (16) 54 °C).

4-Allylthiosemicarbazide, m.p. 95 °C (lit. value (16) 97 °C).

Preparation of Formylferrocene Thiosemicarbazone

Formylferrocene (0.0047 mole) in ethanol (25 ml) was added dropwise to a solution of thiosemicarbazide (0.0047 mole) in water (40 ml). Glacial acetic acid (1 ml) was then added and the resulting mixture was heated on the steam bath for 15 min. The dark-red precipitate which formed when the mixture cooled was collected, washed with aqueous ethanol, dried, and recrystallized repeatedly from ethanol, until pure, m.p. 183 °C (lit. value (2) 190 °C; an incomplete analysis and no infrared spectrum were reported); yield 71%.

Anal. Calcd. for $C_{12}H_{13}N_3SFe$: C, 50.17; H, 4.53; N, 14.63; S, 11.15; Fe, 19.51. Found: C, 49.60; H, 4.54; N, 14.30; S, 11.03; Fe, 20.0.

Preparation of Formylferrocene-substituted Thiosemicarbazones

A solution of formylferrocene (0.0047 mole) in ethanol (25 ml) was added dropwise to a solution of a substituted thiosemicarbazide (0.0047 mole) in ethanol (40 ml). The mixture was heated for 15 min, and then cooled. Water was added until the onset of precipitation and the precipitate which formed was collected, washed with 50% aqueous ethanol solution, dried, and recrystallized until pure. The compounds prepared in this way are listed in Table I.

Preparation of Ethylene Di(formylferrocene Thiosemicarbazone)

A solution of formylferrocene (0.0047 mole) in ethanol

(25 ml) was added dropwise to a solution of ethylene dithiosemicarbazide (7) (0.00235 mole) in dimethylformamide (25 ml). The method was the same as described for the above synthesis and the product was recrystallized repeatedly from dimethylformamide-water mixture, until pure, m.p. 223 °C.

Anal. Calcd. for $C_{26}H_{28}N_6S_2Fe_2$: C, 52.00; H, 4.67; N, 14.00; S, 10.67; Fe, 18.67. Found: C, 51.97; H, 4.63; N, 13.50; S, 10.50; Fe, 19.01.

Preparation of the Copper Complexes of Formylferrocene-substituted Thiosemicarbazones

The general procedure involved the addition of cupric acetate (0.00243 mole) in 25 ml of ethanol, to a warm solution of a formylferrocene-substituted thiosemicarbazone (0.00485 mole) in 30 ml of ethanol. The resulting mixture was refluxed gently for 15 min. The precipitate, which formed after cooling, was removed by filtration, and washed with 3% aqueous hydrochloric acid solution, water, and cold ethanol. The product was dried and recrystallized repeatedly from benzene.

Formylferrocene 4(1-naphthyl)thiosemicarbazone-Cu; m.p. 205 °C.

Anal. Calcd. for $C_{44}H_{36}N_6S_2CuFe_2$: C, 59.49; H, 4.06; N, 9.46; S, 7.22; Cu, 7.21; Fe, 12.53. Found: C, 60.61; H, 4.49; N, 8.96; S, 6.78; Cu, 6.95; Fe, 12.29.

Formylferrocene 4-phenethylthiosemicarbazone-Cu, m.p. 175 °C.

Anal. Calcd. for $C_{40}H_{40}N_6S_2CuFe_2$: C, 56.91; H, 4.74; N, 9.95; S, 7.59; Cu, 7.52; Fe, 13.28. Found: C, 57.03; H, 5.07; N, 10.01; S, 7.43; Cu, 7.36; Fe, 13.78.

Formylferrocene 4-phenylthiosemicarbazone-Cu, m.p. 185 °C.

Anal. Calcd. for $C_{36}H_{32}N_6S_2CuFe_2$: C, 48.58; H, 4.63; N, 12.15; S, 9.26; Cu, 9.20; Fe, 16.19. Found: C, 48.01; H, 3.95; N, 12.26; S, 8.20; Cu, 8.82; Fe, 17.0.

The difficulty experienced in recrystallizing the copper complexes because of their lower solubilities resulted in less satisfactory analyses than were obtained for the parent thiosemicarbazones. Nevertheless, it was felt that these complexes were pure enough for the structural identification purposes for which they were intended.

The infrared spectra of the compounds described in this work were obtained from KBr pellets with a model 21 Perkin-Elmer double-beam spectrophotometer (NaCl prism) over the frequency range 3500 to 700 cm^{-1} . The ultraviolet spectra of the compounds were obtained with either a Cary model 14 or a Beckman DK-1 recording spectrophotometer. All melting points were measured with a Fisher-Johns apparatus and have been corrected. Elemental analyses were performed at the microanalytical laboratory of Drs. Weiler and Strauss in Oxford. The new ferrocene derivatives reported here and the copper complexes of three of them were tested for antifungal activity by a tube dilution method (17). The microorganisms used for this purpose were *Chaetomium globosum*, Strain USDA 1042.4 and *Aspergillus niger*, Strain USDA 215-5373.16.

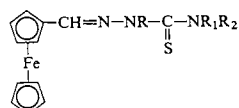
Results and Discussion

Eleven new formylferrocene-substituted thiosemicarbazones which were prepared in this work are listed in Table I. The general structural formula proposed for this series of compounds (A) represents the accepted structure for

TABLE I
 Formylferrocene thiosemicarbazones*

Compound	Substituents	Melting point (°C)	Yield (%)	Formula	Analysis (%)	
					Calculated	Found
1	R = CH ₃ R ₁ = R ₂ = H	185	52†	C ₁₃ H ₁₅ N ₃ SFe	C, 51.82 H, 4.98 N, 13.95 S, 10.63 Fe, 18.61	C, 52.19 H, 4.98 N, 13.75 S, 10.62 Fe, 19.1
2	R = H R ₁ = R ₂ = CH ₃	150	49‡	C ₁₄ H ₁₇ N ₃ SFe	C, 53.33 H, 5.39 N, 13.33 S, 10.16 Fe, 17.78	C, 53.91 H, 5.38 N, 13.20 S, 9.94 Fe, 18.1
3	R = R ₁ = H R ₂ = C ₆ H ₅	197	79‡	C ₁₈ H ₁₇ N ₃ SFe	C, 59.50 H, 4.68 N, 11.57 S, 8.82 Fe, 15.42	C, 59.59 H, 4.80 N, 11.41 S, 8.52 Fe, 16.0
4	R = R ₁ = H R ₂ = 1 - C ₁₀ H ₇	184	81‡	C ₂₂ H ₁₉ N ₃ SFe	C, 63.92 H, 4.60 N, 10.17 S, 7.74 Fe, 13.56	C, 63.66 H, 4.60 N, 9.90 S, 7.80 Fe, 13.7
5	R = R ₁ = H R ₂ = (CH ₂) ₂ C ₆ H ₅	135	76‡	C ₂₀ H ₂₁ N ₃ SFe	C, 61.38 H, 5.37 N, 10.74 S, 8.18 Fe, 14.32	C, 61.09 H, 5.38 N, 10.69 S, 8.05 Fe, 14.7
6	R = R ₁ = H R ₂ = <i>p</i> -NO ₂ C ₆ H ₅	200	81§	C ₁₈ H ₁₆ N ₄ O ₂ SFe	C, 52.94 H, 3.92 N, 13.73 S, 7.84 Fe, 13.73	C, 52.77 H, 3.98 N, 13.80 S, 8.02 Fe, 14.3
7	R = R ₁ = H R ₂ = <i>m</i> -NO ₂ C ₆ H ₅	115	53§	C ₁₈ H ₁₆ N ₄ O ₂ SFe	C, 52.94 H, 3.92 N, 13.73 S, 7.84 Fe, 13.73	C, 52.25 H, 4.07 N, 13.95 S, 7.99 Fe, 14.0
8	R = R ₁ = H R ₂ = CH ₃	138	71†	C ₁₃ H ₁₅ N ₃ SFe	C, 51.82 H, 4.98 N, 13.95 S, 10.63 Fe, 18.61	C, 52.16 H, 5.05 N, 14.05 S, 10.38 Fe, 18.3
9	R = R ₁ = H R ₂ = C ₂ H ₅	146	73	C ₁₄ H ₁₇ N ₃ SFe	C, 53.33 H, 5.39 N, 13.33 S, 10.16 Fe, 17.78	C, 53.38 H, 5.51 N, 12.94 S, 9.95 Fe, 18.3
10	R = R ₁ = H R ₂ = CH ₂ =CHCH ₂	158	51	C ₁₅ H ₁₇ N ₃ SFe	C, 55.05 H, 5.19 N, 12.84 S, 9.78 Fe, 17.13	C, 55.53 H, 5.43 N, 13.00 S, 9.74 Fe, 17.6
11	R = R ₁ = H R ₂ = CH ₃ (CH ₂) ₆	73	75	C ₁₉ H ₂₇ N ₃ SFe	C, 59.22 H, 7.01 N, 10.91 S, 8.31 Fe, 14.55	C, 58.88 H, 7.09 N, 10.85 S, 8.55 Fe, 14.7

*The structural formula may be represented by:



†Recrystallized from ethanol-water.

‡Recrystallized from ethanol.

§Recrystallized from chloroform-hexane.

||Recrystallized from isooctane.

TABLE II
Infrared absorption bands for formylferrocene thiosemicarbazones

Compound number*															
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
3270m 3130w 2930w	3330w† 3120w 2960w	3340w 3140w 2930w	3360m† 3160m 2990w	3360w 3160m 2990w	3340m 3160m 2990w	3340m 3160m 2960w		3380w 3160m 2980w	3380w 3220vw† 3140m 2990w	3350m 3150m 2940s† 2860w	3280w 3160m 2980w	3100m 2960w	3400m	3410m 2940w	3410m 2940w
1610m 1585s	1610m 1535s	1600m 1545s 1510m	1605m 1550s 1500s	1610m 1550s 1500w	1600m 1550s 1510s	1615m 1595w 1535s 1510s	1610m 1555s	1610m 1550s	1645w 1610m	1610m 1600s 1615m	1600s 1540s 1540s		1660w 1615m 1600s	1595s	1600s
1480s 1455w 1440w 1420w	1470m 1455m 1400w	1470sh† 1455m 1405w	1470sh† 1475w 1460w 1440w 1400m	1475w 1460w 1415w	1470sh 1445m 1415w 1400vw	1475w 1445m 1400m	1475w 14395w	1460sh 1415w	1475w 1415br	1470m 1445w 1410w	1465m 1420w 1400w 1390w	1475w 1440w 1415w	1450m 1435w 1400w 1385w	1510s 1450m 1400w 1385w	1505s 1440m 1385w
1385w 1360s 1325w	1375w 1300m	1365br 1320w	1375w 1355w		1340s 1310sh	1355s 1310w	1365w 1310w	1380w 1310m	1375vw 1355vw 1335w	1375w 1355w 1315w 1300w 1280w	1375w 1335m 1290m	1365br 1350m 1330w		1360w 1325w	1315w
1255w	1260w 1230w	1275m	1280m 1260m 1225m	1255m		1275s	1265m	1265m	1280br 1255br 1225s	1280w 1265m 1240w	1255w	1255w	1270w 1250m 1225m	1245m	1250m
1215w 1190w 1110m	1210w	1200m	1170m 1185w 1110m	1185w 1110m	1200s 1210s	1210s	1210w 1160w	1210w 1165w	1190vw 1190w	1110m 1110m 1110m	1110m 1110m	1110m 1110m	1110m 1110m	1110w 1110w	1110w 1110w
1045w 1000s 940w 900w	1030w 1005m 945m	1065br 1060w 1030w 1005m 955w	1060w 1060w 1030w 1005w 945m	1060w 1060br 1030w 1000w 950m	1060w 1030m 1035w 1010m 945m 890w	1060w 1030w 1005w 1010m 945m 845m 825m 795w 760w 740m	1085m 1085w 1030w 1005w 940m	1085w 1030w 1005m 935m	1055m 1030w 1005m 935w	1050w 1035w 1005w 940m	1050w 1030w 1005m 935m 900w	1065w 1030w 1005m 945w 850m 825vw 780m	1070w 1090w 1045w 1005w 855m 820vw 750w 725w	1085w 1050w 1005m 940vw	870vw 820vw 750m 690m

*The numbers 1 to 16 at the head of this table refer to the compounds having the same numbers in Table III.

†The letters following the wave number in the table refer to the band intensity or shape: w, weak; m, medium; vw, very weak; s, strong; sh, shoulder; br, broad.

substituted thiosemicarbazones. Evidence that this structure does, in fact, represent the products reported here, was obtained from the infrared absorption spectra of these compounds. The bands observed in the 3500 to 700 cm^{-1} frequency region are listed in Table II.

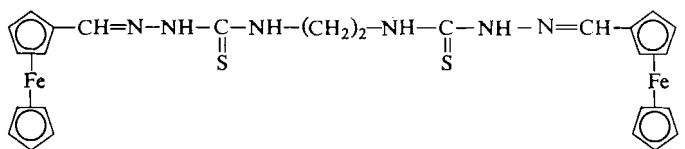
The absorptions characteristic of the expected functional entities for the eleven substituted thiosemicarbazones (Table I), for formylferrocene thiosemicarbazone, and for ethylene di(formylferrocene thiosemicarbazone), are as follows. The bands arising from NH stretching vibrations occur in the 3380 to 3120 cm^{-1} region for all of these compounds. In the 1600 to 1615 cm^{-1} region, the medium to strong band arising from $\gamma(\text{C}=\text{N})$ is observed in all cases. Strong absorption occurs in the 1535 to 1550 cm^{-1} region for compounds **2** to **13** and may be related to the fact that these are *N*-substituted thioamides. The CNH vibration, involving NH bending and C—N stretching (18), gives rise to strong absorption in this region; this has been observed previously in the case of some dithiosemicarbazones of aliphatic and aromatic aldehydes (7). In the spectrum of compound **1**, formylferrocene-2-methylthiosemicarbazone, a strong band appears at 1585 cm^{-1} . This shift to higher frequency has been observed before (19) in a comparison of 2- and 4-substituted thiosemicarbazones. The band which is observed at 1510 or 1500 cm^{-1} in the spectra of compounds **3** to **7** may be attributed to aromatic ring absorptions (see, for example, ref. (20)).

Several absorption bands were observed, in

all the spectra shown in Table II, which are characteristic of formylferrocene or other substituted ferrocenes. Peaks in the vicinity of 1460 (± 20) cm^{-1} and 1410 (± 10) cm^{-1} presumably correspond to the transitions in the ferrocene part of formylferrocene, at 1456 and 1412 cm^{-1} , as described by Rubalcava and Thomson (21). The bands at 1110 cm^{-1} and at 1005 cm^{-1} are also reported for formylferrocene (21) and are described by Rosenblum (22) as characteristic of "ferrocene derivatives possessing an unsubstituted [cyclopentadienyl] ring".

Some of the bands which are observed for the various compounds in the 1030 to 1090 cm^{-1} region presumably represent a contribution from N—C—N stretching vibrations which may be coupled with a small amount of $\gamma(\text{C}=\text{S})$ (23). However, the largest contribution from C=S stretching vibrations gives rise to a band in 830 to 805 cm^{-1} region of the spectra of thiosemicarbazones (23, 24) and presumably accounts for an appreciable proportion of the peaks at 825 to 815 cm^{-1} in the spectra of compounds **1** to **13** (Table II). Superimposed on this in all cases is a contribution from the ferrocene moiety (21).

Collectively, the absorption band assignments described above provide strong evidence that the compounds prepared in this work are indeed the thiosemicarbazones that the analytical data have suggested, and that A represents the correct structure for compounds **1** to **12**. It follows that compound **13**, ethylene di(formylferrocene thiosemicarbazone) could be depicted as



Additional evidence is obtained from the experiments to form copper complexes of some of the thiosemicarbazones. Attempts to prepare copper complexes with 2-substituted thiosemicarbazones failed; only starting materials were recovered from the reaction mixtures. This is in agreement with previous work on copper complex formation with a variety of substituted thiosemicarbazones (19). Copper complexes (2:1) were prepared from compounds **3**, **4**, and **5** (4-substituted compounds) and the infrared spectra of these complexes are given in Table II

(spectra **14** to **16**). Comparison with the spectra of the uncomplexed, parent compounds leads to the following observations. The two bands in NH region of the spectrum have been replaced by a single band in the vicinity of 3410 cm^{-1} , on copper complex formation. In addition, the intensity of the C=N band at about 1600 cm^{-1} has increased, whereas the CNH band at 1550 cm^{-1} has disappeared. Finally, the absorption at 820 cm^{-1} has an appreciably lower intensity. It is reasonable to conclude that complex formation is associated with a reduction in the number

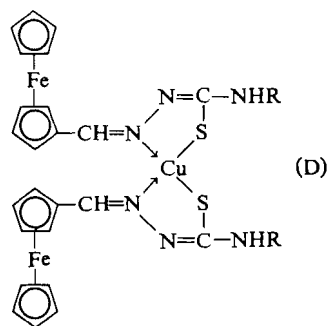
TABLE III
Electronic spectra of formylferrocene thiosemicarbazones

Compound*	Absorption band maxima (mμ) (molar extinction coefficient $\times 10^{-3}$)			Solvent
1	270 (9.6)	312 (30.5)	400 (0.8)	Acetonitrile
2	259 (13.9)	303 (15.7)	—	Acetonitrile
3	272 (15.1)	314 (27.8)	390 (1.1)	Acetonitrile
4	272 (14.5)	313 (29.9)	390 (1.1)	Acetonitrile
5	265 (15.1)	311 (30.9)	390 (1.0)	Acetonitrile
6	273 (21.1)	319 (50.6)	462 (1.3)	Acetonitrile
7	267 (11.4)	316 (40.8)	400 (1.9)	Acetonitrile
8	258 (11.8)	303 (42.0)	448 (1.1)	Acetonitrile
9	262 (13.8)	317 (39.1)	455 (0.9)	Isooctane
10	262 (11.4)	316 (41.8)	456 (1.6)	Isooctane
11	255 (13.4)	308 (48.4)	445 (1.1)	Isooctane
12	270 (11.7)	308 (31.9)	390 (1.1)	Acetonitrile
13	253 (22.1)	313 (35.0)	400 (1.1)	<i>p</i> -Dioxane
14	270 —→	350 (27.2)	444 sh (5.0)	<i>p</i> -Dioxane
15	255 (26.3)	300 (25.3)	440 sh (3.8)	<i>p</i> -Dioxane

* (1) Formylferrocene-2-methylthiosemicarbazone; (2) formylferrocene-4,4-dimethylthiosemicarbazone; (3) formylferrocene-4-phenylthiosemicarbazone; (4) formylferrocene-4-(1-naphthyl)thiosemicarbazone; (5) formylferrocene-4-phenethylthiosemicarbazone; (6) formylferrocene-4-(*p*-nitrophenyl)thiosemicarbazone; (7) formylferrocene-4-(*m*-nitrophenyl)thiosemicarbazone; (8) formylferrocene-4-methylthiosemicarbazone; (9) formylferrocene-4-ethylthiosemicarbazone; (10) formylferrocene-4-allylthiosemicarbazone; (11) formylferrocene-4-heptylthiosemicarbazone; (12) formylferrocene thiosemicarbazone; (13) ethylene di(formylferrocene thiosemicarbazone); (14) copper complex of compound 4; (15) copper complex of compound 5; (16) copper complex of compound 3.

of NH groups, an increase in the number of C=N groups and elimination of the C=S group.

On the basis of this evidence, and in the context of previously proposed structures for copper complexes of analogous compounds (6, 7), it is reasonable to suggest the following general structure for compounds 14, 15, and 16.



In such a 2:1 complex, copper would be paramagnetic. The copper complexes prepared in this work are all strongly paramagnetic, having an electron spin resonance signal intensity of the same order of magnitude as that from an equimolar quantity of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. The g value for compound 15, for example, is 2.066. Thus, there is good reason to believe that the Structure D proposed for the copper complexes, and the Structure A proposed for the thiosemicarbazones, are valid.

The important bands in the electronic absorption spectra of most of the compounds prepared in this work are listed in Table III, together with the relevant molar extinction coefficients. The compounds are all colored and many of them absorb strongly in the important, near-ultraviolet region. However, the requirements for a useful ultraviolet protective substance include, in addition to a high molar extinction coefficient, such considerations as inherent stability, a relatively low volatility and minimal absorption of visible wavelengths. On this simplified basis, it may be suggested that compounds 13, 6, and 3 (in that order) could be useful as retarders of the photooxidation of polymeric materials.

Since some organometallic and many thio-carbonyl-containing compounds have antifungal properties, the formylferrocene thiosemicarbazones and the three copper complexes were evaluated as potential fungicides. Below 1000 p.p.m. none was found effective, in tube dilution tests.

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