[Chem. Pharm. Bull. 25(7)1658—1664(1977)]

UDC 547.831.78.04.08 : 546.982.04

Quinoline-2-thiol Derivatives as Organic Reagents. I.[1] Spectrophotometric Investigations on the Coloration with Some Metal Ions

SABURO NAKANO, TOMOHIKO YOSHIDA, HIROKAZU TANIGUCHI, and NORIKO SUZUKI

Meiji College of Pharmacy[2]

(Received October 20, 1976)

Twenty-nine derivatives of quinoline-2-thiol were synthesized from thiourea and 2-bromo(or 2-chloro)quinoline derivatives. The limit of identification for metal ions with these reagents was examined by a spot test. These reagents gave a precipitate with the following metal ions: Cu^+, Cu^{2+}, Pd^{2+}, Ag^+, Pt^{4+}, Au^{3+}, Hg_2^{2+}, Hg^{2+}, and Bi^{3+}. The effect of substituted groups on molecular extinction coefficient and wavelength of maximum absorption of reagents, of palladium(II) complexes, and of copper(I) complexes was studied. In these reagents, 4-phenyl-7-methoxyquinoline-2-thiol and 4-methyl-8-ethoxyquinoline-2-thiol were the most sensitive reagents for palladium(II) and copper(I) in an acetic acid solution. Extraction of palladium(II) complexes with an immiscible organic solvent was also examined.

Keywords——quinoline-2-thiol derivatives; organic reagent; palladium(II) complex; copper(I) complex; molecular extinction coefficient; coloration

Xavier[3] reported that quinoline-2-thiol (2-mercaptoquinoline, thiocarbostyril) (I) reacted with some metal ions such as palladium(II), copper(II), bismuth(III), mercury(I, II), silver(I), gold(III), platinum(IV), lead(II) (in neutral medium), and thallium(I) (in ammoniacal medium). However, analytical studies on I and its derivatives have not since been made.

We prepared 29 derivatives of I including some known compounds[4] synthesized by the method of Rosenhauer, *et al.*[4b] from thiourea and 2-bromo(or 2-chloro)quinoline derivatives with slight modifications as shown in Chart 1.

As shown in Fig. 1, ultraviolet absorption spectra were different between 1-methyl-2(1*H*)-quinolinethione (Ic) and 2-methylthioquinoline (Id), and the structure of I corresponded

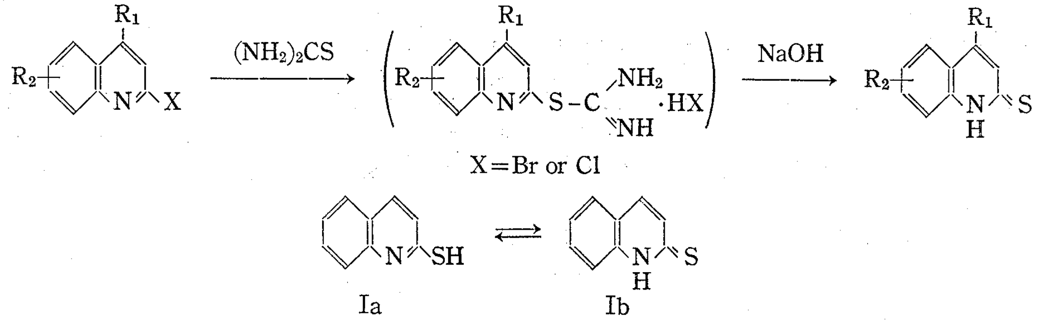


Chart 1

---

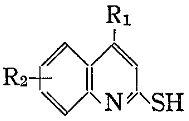
[1] This work was presented at the 82nd, 83rd, and 87th Annual Meetings of the Pharmaceutical Society of Japan, Shizuoka, 1962, Tokyo, 1963, and Kyoto, 1967.

[2] Location: *1-35-23 Nozawa, Setagaya-ku, Tokyo.*

[3] J. Xavier, *Z. Anal. Chem.*, **163**, 182 (1958).

[4] *a*) J. Roos, *Ber.*, **21**, 619 (1888); *b*) E. Rosenhauer, H. Hoffmann, and W. Heuser, *ibid.*, **62**, 2730 (1929); *c*) L. Monti and G. Franchi, *Gazz. Chim. Ital.*, **81**, 764 (1951) [*Chem. Abstr.*, **48**, 3976 (1954)]; *d*) G.F. Duffin and J.D. Kendall, *J. Chem. Soc.*, **1951**, 734; *e*) F. Künzle and J. Schmutz, *Helv. Chim. Acta*, **53**, 798 (1970); *f*) L. Monti, C. Pellerano, and G. Franchi, *Gazz. Chim. Ital.*, **89**, 1084 (1959) [*Chem. Abstr.*, **55**, 536 (1961)]; *g*) D.I. Biskupskaya, *Khim. Geterotsikl. Soedin.*, **1974**, 399.

Table I. Quinoline-2-thiol Derivatives



Compound No.	R_1	R_2	Yield (%)	mp (°C)	Formula	Analysis (%) Calcd. (Found)			UV λ_{max}^{EtOH} nm (log ε)		
						C	H	N			
I	H	H	96	174$^{a)}$	C_9H_7NS	67.05 —	4.38 —	8.69 (8.96)	217 (4.67)	281 (4.30)	389 (4.06)
II	CH_3	H	81	266$^{b)}$ (dec.)	$C_{10}H_9NS$	68.53 —	5.18 —	7.99 (7.90)	218 (4.66)	279 (4.29)	383 (4.01)
III	CH_3	6-CH_3	62	280—281$^{c)}$ (dec.)	$C_{11}H_{11}NS$	69.80 —	5.86 —	7.40 (7.37)	221 (4.74)	285 (4.39)	388 (4.10)
IV	CH_3	7-CH_3	60	279—280 (dec.)	$C_{11}H_{11}NS$	69.80 (69.97)	5.86 (5.85)	7.40 (7.49)	221 (4.77)	278 (4.36)	384 (4.14)
V	CH_3	8-CH_3	75	197—199$^{d)}$	$C_{11}H_{11}NS$	69.80 —	5.86 —	7.40 (7.22)	220 (4.66)	282 (4.42)	385 (4.08)
VI	CH_3	6-C_6H_5	75	264—265 (dec.)	$C_{16}H_{13}NS$	76.46 (76.06)	5.21 (5.13)	5.57 (5.29)	247 (4.39)	295 (4.38)	394 (4.17)
VII	C_2H_5	H	100	210—212 (dec.)	$C_{11}H_{11}NS$	69.80 (69.43)	5.86 (6.12)	7.40 (7.53)	218 (4.73)	279 (4.35)	383 (4.10)
VIII	C_2H_5	6-CH_3	74	220—222 (dec.)	$C_{12}H_{13}NS$	70.89 (69.99)	6.45 (6.61)	6.89 (6.63)	221 (4.71)	285 (4.33)	388 (4.03)
IX	C_2H_5	7-CH_3	64	238—239 (dec.)	$C_{12}H_{13}NS$	70.89 (71.02)	6.45 (6.53)	6.89 (6.86)	222 (4.77)	278 (4.35)	384 (4.12)
X	C_2H_5	8-CH_3	71	154—155	$C_{12}H_{13}NS$	70.89 (70.86)	6.45 (6.38)	6.89 (6.95)	221 (4.71)	282 (4.46)	385 (4.11)
XI	C_6H_5	H	60	222—223$^{e)}$	$C_{15}H_{11}NS$	75.91 (75.51)	4.67 (4.75)	5.90 (6.15)	220 (4.61)	285 (4.43)	396 (4.05)
XII	C_6H_5	6-CH_3	83	247—248 (dec.)	$C_{16}H_{13}NS$	76.46 (76.84)	5.21 (5.44)	5.57 (5.55)	223 (4.61)	290 (4.44)	400 (4.06)
XIII	C_6H_5	7-CH_3	87	234—235	$C_{16}H_{13}NS$	76.46 (76.12)	5.21 (5.48)	5.57 (5.65)	223 (4.65)	284 (4.42)	395 (4.11)
XIV	C_6H_5	8-CH_3	95	187—188	$C_{16}H_{13}NS$	76.46 (76.58)	5.21 (5.37)	5.57 (5.50)	221 (4.57)	287 (4.45)	396 (4.04)
XV	C_6H_5	6-C_6H_5	34	266—267 (dec.)	$C_{21}H_{15}NS$	80.48 (80.16)	4.82 (4.99)	4.47 (4.75)	252 (4.43)	301 (4.49)	406 (4.13)
XVI	H	Benzo[*f*]	66	246 (dec.)	$C_{13}H_9NS$	73.90 (74.00)	4.29 (4.13)	6.63 (6.65)	265 (4.43)	357 (3.85)	408 (3.77)
XVII	CH_3	Benzo[*f*]	83	289—290 (dec.)	$C_{14}H_{11}NS$	74.63 (74.52)	4.92 (4.63)	6.22 (6.37)	263 (4.52)	358 (3.82)	404 (3.89)
XVIII	CH_3	6-CH_3O	75	273—274$^{f)}$ (dec.)	$C_{11}H_{11}NOS$	64.36 (64.33)	5.40 (5.30)	6.82 (6.61)	225 (4.62)	293 (4.39)	400 (4.08)
XIX	CH_3	7-CH_3O	50	244—245$^{g)}$	$C_{11}H_{11}NOS$	64.36 (64.21)	5.40 (5.45)	6.82 (6.69)	226 (4.72)	273 (4.26)	384 (4.24)
XX	CH_3	8-CH_3O	77	193—194	$C_{11}H_{11}NOS$	64.36 (63.96)	5.40 (5.27)	6.82 (6.90)	220 (4.54)	290 (4.50)	386 (4.00)
XXI	CH_3	6-C_2H_5O	81	247—248 (dec.)	$C_{12}H_{13}NOS$	65.72 (65.83)	5.98 (6.26)	6.39 (6.63)	226 (4.63)	293 (4.40)	400 (4.07)
XXII	CH_3	7-C_2H_5O	80	243—244	$C_{12}H_{13}NOS$	65.72 (65.98)	5.98 (6.38)	6.39 (6.88)	227 (4.74)	273 (4.27)	384 (4.26)
XXIII	CH_3	8-C_2H_5O	85	127—128	$C_{12}H_{13}NOS$	65.72 (65.83)	5.98 (6.09)	6.39 (6.61)	220 (4.51)	291 (4.46)	387 (3.96)
XXIV	C_6H_5	6-CH_3O	64	233—234 (dec.)	$C_{16}H_{13}NOS$	71.88 (71.68)	4.90 (5.25)	5.24 (4.97)	228 (4.54)	298 (4.43)	412 (4.05)
XXV	C_6H_5	7-CH_3O	76	251—252	$C_{16}H_{13}NOS$	71.88 (71.83)	4.90 (5.04)	5.24 (5.02)	228 (4.65)	279 (4.41)	396 (4.22)
XXVI	C_6H_5	8-CH_3O	71	197—198	$C_{16}H_{13}NOS$	71.88 (71.95)	4.90 (4.80)	5.24 (5.28)	223 (4.50)	296 (4.54)	400 (3.98)
XXVII	C_6H_5	6-C_2H_5O	81	227—228 (dec.)	$C_{17}H_{15}NOS$	72.57 (72.57)	5.37 (5.45)	4.98 (4.89)	228 (4.54)	298 (4.42)	412 (4.04)

Compound No.	R_1	R_2	Yield (%)	mp (C°)	Formula	Analysis (%) Calcd. (Found)			UV λ_{max}^{EtOH} nm (log ε)		
						C	H	N			
XXVIII	C_6H_5	7-C_2H_5O	71	235—236	$C_{17}H_{15}NOS$	72.57 (73.07)	5.37 (5.38)	4.98 (5.20)	229 (4.64)	278 (4.37)	396 (4.17)
XXIX	C_6H_5	8-C_2H_5O	78	183—184	$C_{17}H_{15}NOS$	72.57 (72.77)	5.37 (5.59)	4.98 (5.37)	223 (4.49)	296 (4.53)	400 (3.97)

a) Lit., mp 174°.4a),4b) *b*) Lit., mp 253°4a); mp 266°.4b) *c*) Lit., mp 280—281°4c); mp 280°.4e) *d*) Lit., mp 195°.4d)
e) Lit., 226—227°.4e) *f*) Lit., mp 276—278°.4f) *g*) Lit., mp 244—245°.4g)

to Ic rather than to Id. Comparison of the spectra of I, Ic, and Id gave evidence that I was a thioketone (Ib).

The yields, mp, elemental analyses, ultraviolet absorption maxima, and molecular extinction coefficients of these derivatives are listed in Table I.

A screening test for 34 kinds of metal ions was carried out by means of a spot test with the above reagents (Table I). These results show that these reagents are excellent as a reagent for palladium (II) and copper(I, II).

The molecular extinction coefficients of complexes of palladium(II) and of copper(I) with I derivatives were calculated from their absorbance in an acetic acid solution and in other organic solvents, and the relation of the coloration between the reagents and metal ions was discussed.

Experimental

General Synthetic Method for Reagents——One mol of 2-bromo(or 2-chloro)quinoline derivatives was added to 1.2 mol of thiourea dissolved in a very small amount of EtOH and the mixture was refluxed on a water bath for 15—30 min. The solution was cooled, diluted to twice its volume, and made alkaline with 10% NaOH solution. The yellowish orange precipitate obtained was collected by filtration, washed with H_2O, and dried. It was recrystallized from EtOH (or benzene) to yellowish orange crystals.

Ic and Id were prepared as described by Albert and Barlin.5)

Apparatus——(1) Spectrophotometric measurements were made with a Shimadzu UV-200 Spectrophotometer and a Hitachi EPS-3T Spectrophotometer. (2) The pH measurements were made with a Tōa HM-20A pH-meter.

Metal Solution——Palladium(II) Solution (1 mg/ml): $PdCl_2$ (1.6670 g) was dissolved in 20 ml of conc. HCl and diluted with redistilled H_2O to 1000 ml in a measuring flask. The concentration of palladium(II) in this solution was checked by a gravimetric method using dimethylglyoxime.

Copper(II) solution (5 mg/ml): $CuSO_4 \cdot 5H_2O$ (9.9229 g) was dissolved in a suitable volume of 0.1 N H_2SO_4 and diluted with redistilled H_2O to 500 ml in a measuring flask. The concentration of copper(II) in this solution was checked by titration with 0.01 N disodium ethylenediaminetetraacetate.

Copper(I) solution (0.5 mg/ml): To 5 mg/ml of the copper(II) solution, 10 g of $NH_2OH \cdot HCl$ was added to reduce to Cu^+, and diluted with redistilled H_2O to 100 ml in a measuring flask. The concentration was checked by a gravimetric method using KSCN.

Stock solution of other metal ions: The following metal ions were used for the spot test: Li^+, Na^+, Mg^{2+}, Al^{3+}, K^+, Ca^{2+}, Cr^{3+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Zn^{2+}, As^{3+}, Sr^{2+}, Ag^+, Cd^{2+}, Sn^{2+}, Sb^{3+}, Ba^{2+}, Ce^{4+}, W^{4+}, Pt^{4+}, Au^{3+}, Hg_2^{2+}, Hg^{2+}, Tl^+, Pb^{2+}, Bi^{3+}, Th^{4+}, and U^{6+}.

All chemicals and solvents used were of reagent grade.

Reagent Solution——Derivatives (0.1 g) of I were dissolved in glacial AcOH to make a 0.1% (w/v) reagent solution.

Spot Test for Metals——The spot test was carried out using a spot plate. A drop of the test solution containing a metal ion and a drop of the reagent solution were placed in the depression and the two drops were mixed by means of a glass rod. After about 1 min, the color developed was observed against a blank. The color of reagent blank was pale yellow. The limit of identification was expressed as μg/ml.

Measurement of Molecular Extinction Coefficient——(1) A mixture of 2 ml of palladium(II) solution (1.0, 1.3, 2.0, 2.5, and 5.0 μg/ml), 3.3 ml of glacial AcOH, and 1.0 ml of 0.002 M of the reagent solution was

---

5) A. Albert and G.B. Barlin, *J. Chem. Soc.*, **1959**, 2384.

allowed to stand at room temperature (20°) for 10 min and absorption spectrum (Fig. 2) of the reaction mixture was measured with a 1-cm cell, relative to a reagent blank. (2) The same measurement was made with 2 ml of copper(I) solution (5.0 μg/ml) (Fig. 3). Their results are shown in Table III.

Preparation of Palladium Complexes——Method A: A solution of derivatives (4×10^{-4} mol) of I in 40 ml glacial AcOH was added to 20 ml of 0.01 M $PdCl_2$ solution, and the mixture was allowed to stand overnight. The reddish brown precipitate formed was collected by filtration, washed with 60% AcOH and EtOH, and dried *in vacuo* for 2 days (63 mg, 38%).

Method B: A mixture of 10 ml of 0.01 M $PdCl_2$ solution and 10 ml of redistilled H_2O was added to 40 ml glacial AcOH containing about a 10-fold molar (0.001 M) excess of I. The solution was allowed to stand at room temperature for 2 days. The red precipitate was collected by filtration, washed with AcOH and redistilled H_2O, and dried *in vacuo* for 2 days (quantitative yield).

Extraction of Palladium Complexes——To 20 ml of palladium solution (1 μg/ml), 5 ml of buffer solution was added to adjust to an optimum pH (about 3). The solution was shaken with 5 ml of an organic solvent containing 0.05% of the reagent for 10 min. The organic layer was diluted with the reagent solution to 5 ml in a measuring flask. The organic layer was filtered through a cotton wool and absorbance of the filtrate was measured, relative to a reagent blank.

Results and Discussion

Solubility of Reagents

I is soluble in dichloromethane, chloroform, N,N′-dimethylformamide, and acetic acid, sparingly soluble in ethylene dichloride, slightly soluble in *o*-dichlorobenzene, chlorobenzene, benzene, and ethanol, very slightly soluble in ether and carbon tetrachloride, and insoluble

TABLE II. Limit of Identification of Metal Ions (μg/ml)

Compound No.	$Cu^{+a)}$	$Cu^{2+a)}$	$Pd^{2+a)}$	$Ag^{+b)}$	$Pt^{4+a)}$	$Au^{3+a)}$	$Hg_2^{2+b)}$	$Hg^{2+b)}$	$Bi^{3+a)}$
I	5	5	1	400	10	100	80	200	100
II	1	0.5	1	400	5	100	50	200	50
III	1	1	1	400	5	100	80	200	30
IV	1	1	1	300	10	100	50	100	30
V	0.5	0.5	1	300	10	50	80	200	10
VI	0.5	0.5	0.5	200	10	50	80	80	5
VII	1	1	1	400	5	100	80	200	100
VIII	1	0.5	1	200	5	50	80	100	30
IX	1	1	1	200	10	100	100	200	30
X	0.5	0.5	1	200	5	50	100	200	10
XI	1	1	1	200	10	50	80	200	5
XII	0.5	1	1	200	10	80	80	100	5
XIII	0.5	1	0.5	200	5	80	200	100	5
XIV	0.5	1	1	200	10	50	200	200	5
XV	0.5	1	0.5	100	10	50	100	100	5
XVI	1	1	1	200	10	50	100	80	10
XVII	1	1	0.5	200	10	80	80	80	5
XVIII	1	1	1	100	5	50	80	50	100
XIX	1	1	0.5	200	10	30	200	100	100
XX	0.5	0.5	1	100	10	30	200	100	20
XXI	1	1	0.5	200	5	30	100	100	100
XXII	0.5	1	0.5	200	10	30	100	100	100
XXIII	0.5	0.5	1	100	10	30	200	50	10
XXIV	1	1	1	100	10	30	200	200	5
XXV	1	1	0.5	200	10	50	200	100	5
XXVI	0.5	0.5	1	100	10	50	200	80	10
XXVII	1	1	0.5	80	10	50	200	100	5
XXVIII	1	1	0.5	200	30	50	200	100	5
XXIX	0.5	1	1	80	30	50	200	80	30

a) Coloration: orange-yellow.
b) Colorless.

in water. Solubility of the derivatives of I was inversely proportional to the increase in their mp.

Stability of Reagents

I is more stable than quinoline-8-thiol which shows depression of mp and color change with passage of time in the solid state. On the other hand, I and quinoline-8-thiol hydrochloride had a similar stability in ethanol. The absorbance (in EtOH) of 0.01 mM solution of these reagents decreased about 5.2—5.5% after 1 week. Also, the absorbance (in AcOH) of 0.01 mM solution of I and XXV decreased about 5.5% in 4 days and an inconstant decrease was observed, thereafter.

Reaction with Metal Ions

The metal ions which gave a colored precipitate with these reagents in an acetic acid solution were as follows: Copper(I), red; copper(II), orange; palladium(II), reddish brown; silver(I), white; platinum(IV), yellow; gold(III), yellow; mercury(I), white; mercury(II), white; bismuth(III), yellow. All the reagents (Table I) exhibited almost the same reaction.

The limit of identification by means of the spot test is shown in Table II. These results showed that the limit of identification for palladium(II), copper(I), and copper(II) was definitely better than that of other metal ions.

Table III. UV maximum and log ε of Complexes of Pd^{2+} and Cu^{+} with Quinoline-2-thiol Derivatives

Compound No.	Pd^{2+} $\lambda_{\max}^{\mathrm{AcOH}}$ (log ε)	Cu^{+} $\lambda_{\max}^{\mathrm{AcOH}}$ (log ε)
I	418(4.48)	423(4.13)
II	414(4.51)	420(4.08)
III	416(4.52)	424(4.11)
IV	411(4.57)	419(4.19)
V	412(4.49)	432(4.26)
VI	426(4.70)	441(4.20)
VII	410(4.52)	419(4.17)
VIII	416(4.51)	428(4.11)
IX	411(4.58)	421(4.19)
X	412(4.57)	433(4.30)
XI	426(4.55)	448(3.89)
XII	429(4.57)	452(3.92)
XIII	426(4.58)	445(4.02)
XIV	427(4.55)	448(4.25)
XV	439(4.69)	463(4.32)
XVI	435(4.69)	443(3.89)
XVII	427(4.68)	459(3.90)
XVIII	427(4.55)	438(3.91)
XIX	413(4.72)	422(4.10)
XX	418(4.37)	430(4.16)
XXI	427(4.56)	439(3.99)
XXII	413(4.61)	420(4.19)
XXIII	415(4.44)	433(4.34)
XXIV	440(4.55)	467(3.88)
XXV	426(4.78)	440(4.03)
XXVI	431(4.42)	450(4.16)
XXVII	441(4.59)	470(3.90)
XXVIII	427(4.75)	451(4.03)
XXIX	428(4.47)	453(4.30)

Effect of Substituent Groups and Their Position on Molecular Extinction Coefficient

From Table III, the molecular extinction coefficient (ε) of palladium(II) complexes of the substituted I decreased in the order of (1) 4-phenyl, 4-ethyl, 4-methyl, unsubstituted I; and (2) 4-phenyl(or 4-methyl)-7-substituted, 4-phenyl (or 4-methyl)-6-substituted, 4-phenyl-(or 4-methyl)-8-substituted compounds.

These orders of decrease in (2) above, and (4) and (6) below apply only when the substituents (methyl, methoxyl, and ethoxyl) are the same in 6-, 7-, and 8-positions; *e.g.*, methyl as a substituent in 6, 7, 8.

Consequently, the molecular extinction coefficient of palladium(II) complex of 4-phenyl-7-methoxyquinoline-2-thiol (XXV) was the highest (ε 59580 at 426 nm, log ε 4.78).

On the other hand, the molecular extinction coefficient of copper(I) complexes of the substituted I decreased in the order of (3) 4-ethyl, unsubstituted, 4-methyl, 4-phenyl substituted I; and (4) 4-methyl(or 4-phenyl)-8-substituted, 4-methyl(or 4-phenyl)-7-substituted, 4-methyl-(or 4-phenyl)-6-substituted compounds.

Consequently, the molecular extinction coefficient of copper(I) complex of 4-methyl-8-ethoxyquinoline-2-thiol (XXIII) was the highest (ε 22120 at 433 nm, log ε 4.34).

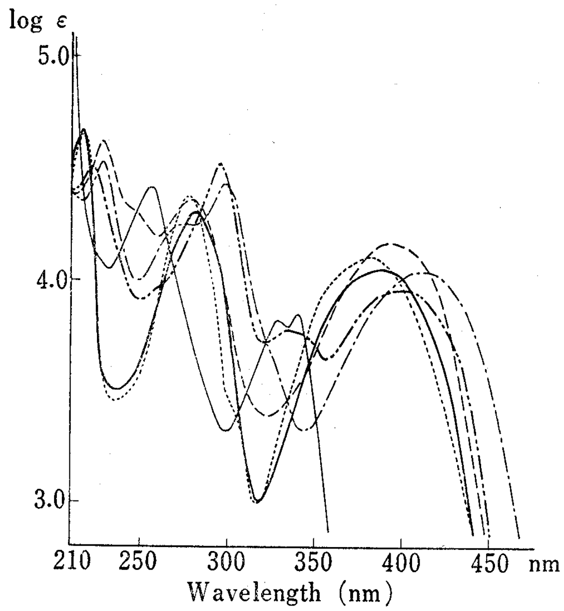


Fig. 1. Ultraviolet Spectra of Quinoline-2-thiol Derivatives (in EtOH)

━━, I; —-—, XXVII; ------, XXVIII;
—··—, XXIX; ········, I-c; ——, I-d.

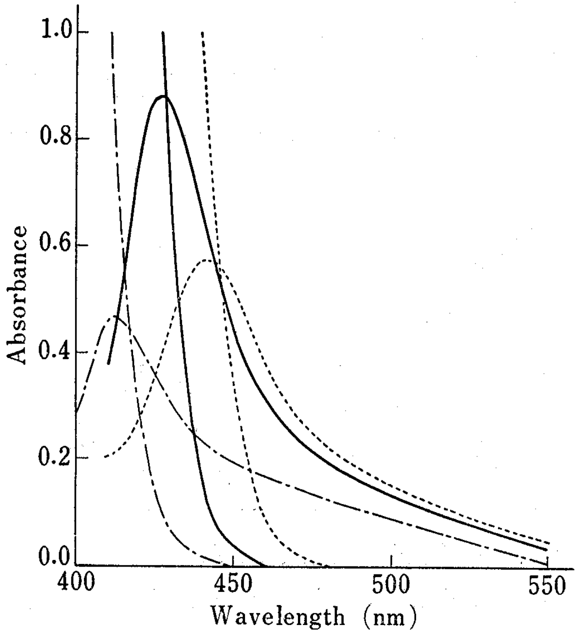


Fig. 2. Absorption Spectra of Complexes of Pd(II) with Quinoline-2-thiol Derivatives (in AcOH Solution)

Pd: 1.49×10^{-5} mol/liter.
—-—, IV; ········, XXVII; ——, XXVIII.

Effect of Substituent Groups and Their Positions on Wavelength of Maximum Absorption

The wavelength of maximum absorption ($\lambda_{\max}^{\mathrm{EtOH}}$) of these derivatives of I decreased in order of (5) 4-phenyl, unsubstituted, 4-methyl, 4-ethyl substituted I; and (6) 4-phenyl(or 4-methyl)-6-substituted, 4-phenyl (or 4-methyl)-8-substituted, 4-phenyl(or 4-methyl)-7-substituted compounds.

The above relations were also found to hold for the order in the wavelength of maximum absorption of the complexes of palladium(II) and of copper(I) with these reagents in an acetic acid solution (Figs. 2 and 3), but the absorption maximum of copper(I) complexes of III, IV, and V did not follow the above order (6).

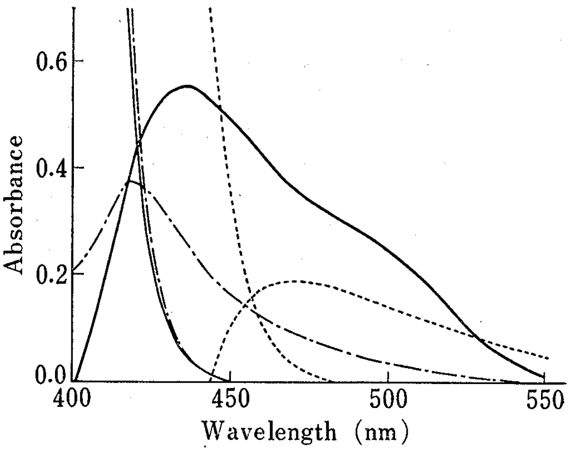


Fig. 3. Absorption Spectra of Complexes of Cu(I) with Quinoline-2-thiol Derivatives (in AcOH Solution)

Cu: 2.50×10^{-5} mol/liter.
—-—, IV; ——, XXIII; ········, XXVII.

Molar Composition of Complexes

The palladium(II) complexes of pyridine-2-thiol, N,N′-disubstituted thiourea, and pyrimidinethiol derivatives have been reported by Evans and Wilkinson,[6] Tarantelli and Furlani,[7] and very recently by Singh and Katyal,[8] respectively.

---

6) I.P. Evans and G. Wilkinson, *J. Chem. Soc.*, **1974**, 946.
7) T. Tarantelli and C. Furlani, *J. Chem. Soc.*, **1968**, 1717.
8) A.K. Singh and M. Katyal, *Talanta*, **23**, 337 (1976).

The molar composition of palladium(II) complexes of some I derivatives was established from elemental analyses (Table IV), continuous variation method, and molar ratio method. The ratio of palladium(II) and I derivatives was approximately 1: 2 (from method A) and 1: 4 (from method B).

The linkage of the metals and reagents will be discussed in a separate paper.

Table IV. Complexes of Palladium with Quinoline-2-thiol Derivatives

Compound No.	Method	Formula	Analysis (%) Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N
I	A	$Pd(C_9H_7NS)_2Cl_2$	43.26	2.82	5.60	41.94	2.60	5.22
I	B	$Pd(C_9H_7NS)_4Cl_2$	52.59	3.43	6.81	50.86	3.77	6.21
XI	A	$Pd(C_{15}H_{11}NS)_2Cl_2$	55.27	3.40	4.29	56.17	3.41	4.23
XXV	A	$Pd(C_{16}H_{13}NOS)_2Cl_2$	53.98	3.68	3.93	55.82	3.74	3.80
XXIX	A	$Pd(C_{17}H_{14}NOS)_2Cl_2$	55.18	4.09	3.79	53.76	4.13	3.96

Extraction of Palladium Complexes

The palladium(II) complex of I was extractable from aqueous solution through the use of the following immiscible solvents. The log ε (λ_{max} nm) of palladium(II) complex of I in dichloromethane, ethylene dichloride, chloroform, *o*-dichlorobenzene, benzene, and chlorobenzene were respectively 4.07(456), 3.96(459), 3.92(448), 3.72(455), 3.68(453), and 3.60(453). Also, the log ε ($\lambda_{max}^{CH_2Cl_2}$ nm) of palladium(II) complexes of XXV, IV, III, V, and XXIII were respectively 4.18(462), 4.11(454), 4.10(460), 3.94(443), and 3.81(437).

These results indicate that I and its derivatives exhibit a high sensitivity for palladium(II) compared with quinoline-8-thiol (XXX), because the log ε of palladium(II) complex of XXX in acetic acid and chloroform were 3.85 and 3.78, respectively.

We have found that XXV and XXIII will serve for the detection or spectrophotometric determination of palladium and copper, and that derivatives of I will serve for the extraction determination of palladium with immiscible solvents.

Acknowledgement The authors thank Mrs. Miyako Sazanami and an all the staff of the Central Instrument Room of this College for elemental analyses.