The Analytical Application of Sulfur Analogues of β-Diketones. III. The Separation of Cobalt(II), Nickel(II), Copper(II), Zinc(II), Mercury(II), Lead(II), and Cadmium(II) as Their STTA (1,1,1-Trifluoro-4-(2-thienyl)-4-mercapto-3-buten-2-one) Complexes by Thin-layer Chromatography on Silica Gel

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Cobalt(II), nickel(II), copper(II), zinc(II), mercury(II), lead(II), and cadmium(II) were extracted with STTA (1,1,1-trifluoro-4-(2-thienyl)-4-mercapto-3-buten-2-one) in cyclohexane, and their colored complexes were chromatographed on a thin-layer of silica gel with various organic solvents. The developing solvents used were 18 kinds of pure solvents and 10 different binary solvent mixtures of 1 : 1, v/v. An excellent separation could be achieved after development with carbon tetrachloride, carbon disulfide, ethyl acetate, and cyclohexane–chloroform, chloroform–carbon disulfide, and carbon tetrachloride–carbon disulfide mixtures. The R_f value generally increased in the following orders: Cd(II), Zn(II), Pb(II), (STTA)<Hg(II)<Co(II, III)<Cu(II)<Ni(II) (with carbon tetrachloride); Cd(II), Zn(II), Pb(II), (STTA)<Co(III)<Hg(II)<Cu(II)<Ni(II) (with carbon disulfide); Cd(II), (STTA)<Zn(II)<Pb(II)<Hg(II), Co(III), Cu(II), Ni(II) (with ethyl acetate); and Cd(II), Zn(II), Pb(II), (STTA)<Hg(II)<Co(III)<Cu(II)<Ni(II) (with the cyclohexane–chloroform, chloroform–carbon disulfide, and carbon tetrachloride–carbon disulfide mixtures). A few μg $Ni(STTA)_2$ chelates on the plate could be determined quantitatively by measuring the spot area from the curve drawn on a millimeter-graph sheet after driving a densitometer across the spot. Some aspects of the behavior of the STTA chelates on the thin-layer of silica gel have also been discussed.

Thin-layer chromatography (tlc) has recently become popular in the separation of a wide variety of organic and inorganic substances, using the standardized procedures of Stahl and others.[1] Taking advantage of this technique, the separation of the metals as their chelates has been performed with several extracting reagents, such as acetylacetone,[2–4] α-nitroso-β-naphthol,[5] 8-hydroxyquinoline,[6] dithizone,[7–12] and diethyldithiocarbamic acid.[13–17] A new chelating reagent, 1,1,1-trifluoro-4-(2-thienyl)-4-mercapto-3-buten-2-one (abbreviated as STTA), has been found to form stable and extractable chelates with a specific color,[18] and it has been used for several analytical purposes, *e.g.*, the spectrophotometric determination of cobalt(II),[19] and the separation of Hg, Co, and Zn by extraction chromatography.[20] However, the STTA chelates have not yet been submitted to thin-layer chromatography. In the present investigations, the metal ions were extracted in cyclohexane containing STTA, and the STTA chelates thus formed were chromatographed on the thin-layer of silica gel using various organic solvents. The possibility of the quantitative determination and the mutual separation of these metal complexes has been investigated; some aspects of the chromatographic behavior of the STTA chelate have also been discussed.

Experimental

Apparatus. The thin-layer chromatograph: TLC "Sandwich" developing apparatus, model TL-IS, of Yamato Scientific Instruments. Densitometer: Atago self-recording densitometer designed for paper electrophoretic patterns.

Materials. Metal ions: Metal salts, $CoCl_26H_2O$, $NiCl_26H_2O$, $CuSO_45H_2O$, $ZnCl_2$, $HgCl_2$, $Pb(NO_3)_2$, and $CdCl_2$, were dissolved in distilled water or in a slightly acidic solution to make a 10^{-1} M aqueous solution of each metal ion.

STTA: STTA was prepared by a modification of the method of Berg and Reed.[19]

Adsorbent: Silica gel for the thin-layer chromatography, WAKOGEL B-5 (binder, $CaSO_41/2H_2O$, 5%).

Developing solvents: Methanol, ethanol, cyclohexanol, acetone, methyl ethyl ketone, ethyl acetate, ethyl ether, carbon tetrachloride, chloroform, ethylene chloride, carbon disulfide, *n*-hexane, cyclohexane, benzene, xylene (bp 138.5—141.5 °C), nitrobenzene, *o*-dichlorobenzene, and benzonitrile were all of reagent-grade materials and were purified by the ordinary method, if necessary.

Solvent Extraction. The experimental procedure for the solvent extraction of trace amounts of metals was almost

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the same as has previously been described.[19,21] The sample solutions for the thin-layer chromatography were metal-STTA chelates in cyclohexane, which were prepared as follows: a 10^{-2} M salt solution was acidified with 0.1 M acetic acid to pH 6.0—6.5 and then this solution was shaken with 10^{-3} M STTA in cyclohexane for 1.5 hr. After the extraction, some deposit in a membrane substance at the interface of the phases was found in the cases of Co, Cu, and Hg. Zinc and Ni gave no precipitate, while Pb and Cd gave insoluble chelates in cyclohexane, but soluble ones in ethyl acetate.

Thin-layer Chromatography A homogeneous paste was prepared by thoroughly mixing 30 g of the silica gel with 60 ml of distilled water in a mortar using a pestle. Then, the paste was spread on a 20×20 cm glass plate at a thickness of 0.25 mm using a commercial applicator. The plates were air-dried for 20—30 min at room temperature; then they were activated at 110 °C for 60 min and cooled overnight in a desiccator containing silica gel. By means of an micropipet, a 3-μl portion of a sample solution was placed as a spot on thin-layer at definite intervals within about 1.5 cm from the bottom of the plates. The spots were then air-dried at room temperature. Both sides of the chromatoplates were covered with glass plates to form a kind of sandwich; the plates were firmly held with clips. This "sandwich" was placed in a chromatographic chamber containing an organic solvent or some mixed solvents and was dipped into the solvent up to 1 cm below the sample spots. The organic solvent was allowed to proceed up to about 10 cm of the sample spot, and then the plates were taken out of the chambers and exposed to air. No spraying was necessary for the detection, since most of the chelates show different, characteristic colors. Development on a chromatoplate coated with silica gel was carried out at room temperature (22—26 °C).

The R_f value of the substances, the relative migration rates of the solutes, is one of the most convenient expressions of the position of the compounds on the chromatoplate, where:

$$R_f = \frac{\text{distance traveled by the substance}}{\text{distance traveled by the solvent}}$$

Moreover, the R_f value is a measure of the interaction among solute, solvent, and adsorbent, and is reproducible and characteristic for each solute in a given solvent-adsorbent system under specified conditions.

Results and Discussion

Extraction. The metal ions were extracted in trace amounts with 10^{-3} M STTA in cyclohexane; their extraction curves are presented in Fig. 1. It was found that the quantitative extractions of the STTA chelates of Co(II), Ni(II), Cu(II), Zn(II), Hg(II), Pb(II), and Cd(II) were almost achieved in the pH region below 7. The extraction of cobalt seemed to be accompanied by the transformation of $Co(STTA)_2$ to $Co(STTA)_3$.[19-21]

Absorption Spectra. The absorption spectra of STTA and its metal chelate in cyclohexane are shown in Fig. 2. Each chelate showed its own specific color, had an absorption maxima, and was stable for at least 7 days. These results are summarized in Table 1. The compounds could be identified only by observing the individual specific color on the chromatoplates.

Development and Separation of the STTA Chelates with

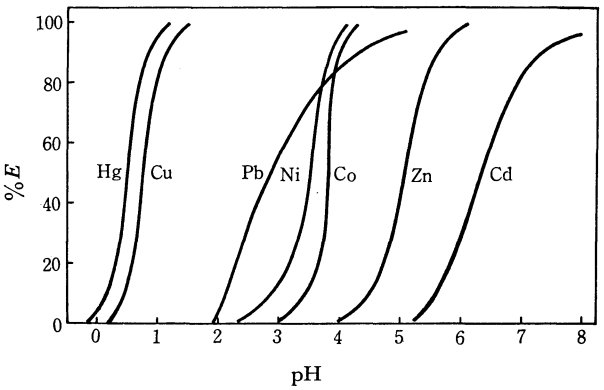

Fig. 1. Extraction curves of metal STTA chelates.
Metal: trace, STTA: 10^{-3} M, Diluent: cyclohexane, Shaking time: 15—30 min.

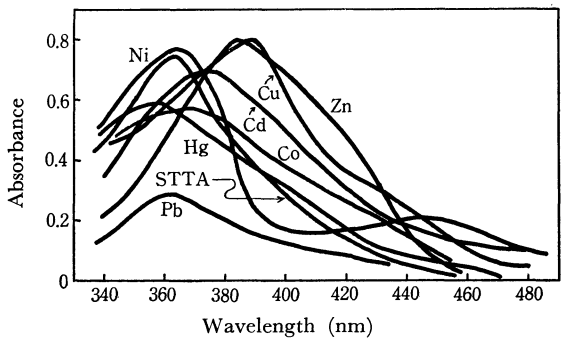

Fig. 2. Absorption spectra of STTA and its metal chelates in cyclohexane and ethyl acetate against the same organic solvent.
STTA, chelate: *ca.* 4×10^{-5} M, Diluent: cyclohexane (Co, Ni, Cu, Zn, Hg), ethyl acetate (Pb, Cd)

Table 1. Color and absorption maxima of STTA and its metal chelates in cyclohexane

Compound	Color	Absorption maxima (nm)
STTA	Reddish yellow	365, 361[a]
$Co(STTA)_3$	Brown	367
$Ni(STTA)_2$	Reddish brown	366, 450
$Cu(STTA)_2$	Olive brown	389
$Zn(STTA)_2$	Bright yellow	387
$Hg(STTA)_2$	Pale yellow	357
$Pb(STTA)_2$	Orange red	365[a]
$Cd(STTA)_2$	Yellow	375[a]

a) Diluted with ethyl acetate.

Pure Solvents. Some representative results of the development of STTA and its metal STTA chelate with individual solvents on a thin-layer of silica gel by the ascending method are given in Table 2. The chelates may be classified into four groups by chromatographic behavior: 1) Chelates which do not migrate from the sample spot (with cyclohexane and *n*-hexane). 2) Chelates which can be developed to a moderate distance over a comparatively wide range (with methanol, carbon tetrachloride, and carbon disulfide). 3) Chelates which move up to the solvent front (with ethanol, acetone, methyl ethyl ketone, ethyl acetate, chloroform, ethylene chloride, benzene, xylene, nitrobenzene, *o*-dichlorobenzene, and benzonitrile).

21) T. Honjo, S. Yashima and T. Kiba, *ibid.*, 3772, (1973).

Table 2. R_f values of STTA and its metal STTA chelates with various developing pure solvent on silica gel

Developing solvent	Dielectric constant	Developing length (cm)	Developing time (min)	Metal							
				Co	Ni	Cu	Zn	Hg	Pb	Cd	STTA
Methanol	32.6	8.8	60	0.23	0.36	0	0	0.07	0	0	0
Ethanol	24.3	10.7	90	1.00	1.00	1.00	1.00	1.00	a)	a)	1.00
Cyclohexanol	15.0	5.5	555	a)	a)	a)	a)	a)	a)	a)	a)
Acetone	20.7	9.5	15	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Methyl ethyl ketone	18.5	10.4	20	1.00	1.00	a)	a)	1.00	a)	a)	a)
Ethyl acetate	6.0	9.75	37	1.00	0.91	1.00	0.71	1.00	0.73	0.47	0.91
Diethyl ether	4.3	9.9	20	a)	a)	a)	a)	0.92	a)	a)	a)
Carbon tetrachloride	2.2	10.0	70	0.35	0.51	0.36	0	0.17	0	0	0
Chloroform	4.8	12.2	55	0.90	0.96	0.94	0.03	0.90	0.02	0.02	0.02
Ethylene chloride	10.4	10.5	40	1.00	1.00	1.00	0.04	1.00	0.04	0.04	0.04
Carbon disulfide	2.6	9.7	20	0.16	0.40	0.25	0	0.17	0	0	0
n-Hexane	1.9	11.2	40	0.02	0.05	0.02	0	0	0	0	0
Cyclohexane	2.0	9.55	50	0	0	0	0	0	a)	a)	0
Benzene	2.3	10.0	36	1.00	0.99	0.99	0	a)	a)	a)	0
Xylene	2.6	10.0	40	0.85	0.81	0.78	a)	0.76	a)	a)	a)
Nitrobenzene	34.8	11.5	60	1.00	1.00	1.00	0.05	1.00	a)	a)	0.06
o-Dichlorobenzene	9.9	12.4	60	0.83	0.90	0.83	0.01	0.69	0.02	0.02	0.02
Benzonitrile		11.6	60	1.00	1.00	1.00	0.27	1.00	a)	a)	0.24

a) The spots disappeared during the development. The average deviation of R_f values was 0.01.

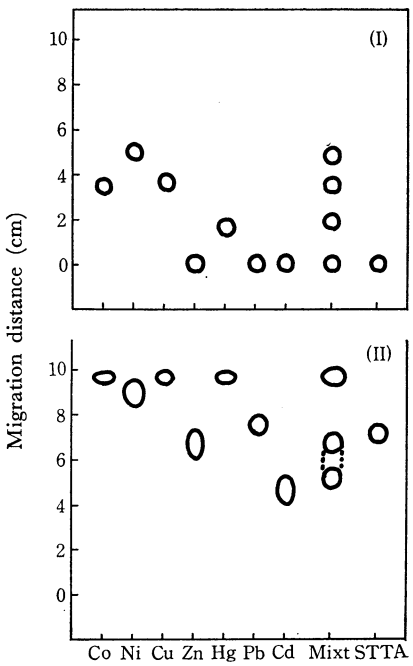

Fig. 3. Chromatogram of STTA and its metal chelates with single component solvent.
STTA, Chelate: *ca.* 5×10^{-4} M (3 μl); Developing solvent: (I) carbon tetrachloride, (II) ethyl acetate

4) Chelates which dissolve in the solvent and the spots of which disappear during development (with cyclohexanol and diethyl ether). The times required for about a 10 cm(8.7—12.4 cm) development were all about 15—90 min. The R_f values of the STTA chelates generally increased in the order of: Cd(II)<Zn(II)< Pb(II), (STTA)<Hg(II)<Co(II, III)<Cu(II)<Ni-(II). With such developing solvents as carbon tetrachloride, carbon disulfide, and ethyl acetate, the mutual separation of various metal chelates was achieved successfully. Some representative chromatograms of STTA and its metal chelates with carbon tetrachloride and ethyl acetate are shown in Fig. 3. It was observed that the cobalt-STTA chelate extracted in high concentrations as 30 μl of a 4×10^{-5} M chelate solution gives two spots; one may possibly correspond to Co-$(STTA)_2$ (R_f=0.29), and the other, to $Co(STTA)_3$ (R_f=0.35), using carbon tetrachloride. The elution power of a solvent is generally related to its dielectric constant or its dipole-dipole moment. The greater the polarity of the solvent, the greater the distance of the development on the chromatographic plate. The eluotropic series of solvents proposed by Trappe[22] and by Strain[23] may be valid also with regard to the thin-layer chromatographic behavior of the STTA chelates.

Development and Separation of the STTA Chelates with a Binary Solvent Mixture. By using a binary mixture of solvents in a 1 : 1 volume ratio, STTA and its metal STTA chelates were developed; some representative results are shown in Table 3. All the mix ed solvents could develop the STTA chelates to a moderate distance. Among these mixed solvents, the pairs of cyclohexane–chloroform, chloroform–carbon disulfide, and carbon tetrachloride–carbon disulfide were most suitable for the mutual separation of the STTA chelates. Some representative chromatograms of STTA and its metal chelates with carbon tetrachloride, carbon disulfide, and cyclohexane–chloroform mixtures are shown

22) W. Trappe, *Biochem, Z.*, **305**, 150 (1940); **306**., 316 (1940).
23) H. H. Strain, "Chromatographic Adsorption Analysis," Interscience Publ. Inc., New York (1942) p. 66.

TABLE 3. R_f VALUES OF STTA AND ITS METAL STTA CHELATES WITH VARIOUS MIXED DEVELOPING SOLVENTS ON SILICA GEL

Developing solvent (1 : 1, v/v)	Developing length (cm)	Developing time (min)	Metal					
			Co	Ni	Cu	Zn	Hg	STTA
Cyclohexane-ethanol	10.75	180	0.84	0.84	0.84	0.82	a)	0.84
Cyclohexane-chloroform	9.20	45	0.72	0.79	0.77	0	0.62	0
Cyclohexane-benzene	9.8	35	0.63	0.73	0.64	0	a)	0
Benzene-methanol	9.3	48	0.77	0.77	0.78	0.69	0	0
Benzene-chloroform	9.6	42	0.95	0.97	0.95	0	0.85	0
Benzene-carbon tetrachloride	9.3	40	0.81	0.84	0.79	0	0.68	0
Benzene-carbon disulfide	9.7	23	0.80	0.83	0.82	0	0.74	0
Chloroform-carbon tetrachloride	8.7	45	0.78	0.85	0.78	0	0.64	0
Chloroform-carbon disulfide	9.5	23	0.68	0.89	0.86	0.15	0.71	0.06
Carbon tetrachloride-carbon disulfide	9.3	26	0.35	0.56	0.40	0	0.25	0

a) The disappeared spots during development. The average deviation of R_f values was 0.01.

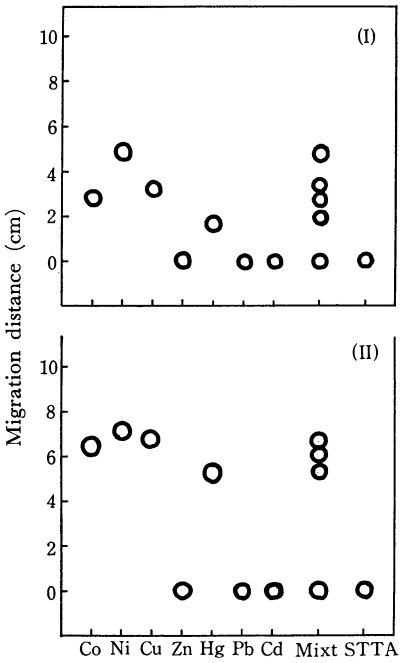

Fig. 4. Chromatogram of STTA and its metal chelates with binary solvent mixture.
STTA, Chelate: *ca.* 5×10^{-4} M (3 μl)
Developing solvent: (I) carbon tetrachloride-carbon disulfide, (II) cyclohexane-chloroform

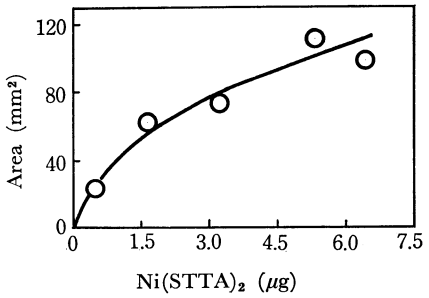

Fig. 5. Calibration curve of a thin layer chromatogram of $Ni(STTA)_2$ chelate obtained by photodensitometry.
Developing solvent: carbon tetrachloride

in Fig. 4. The R_f values of all the STTA chelates with the binary solvent mixtures had the same tendency to increase in the order of Zn(II)<Hg(II)<Co(III)<Cu(II)<Ni(II) as in the case of the single solvents. In the case of the mixed solvents, some demixing may occur, accompanied by some changes in the solvent ratio, because of the difference in the adsorbability of each solvent on the silica gel; therefore, the developed spots are believed to give suitable R_f values, separated from each other.

Quantitative Evaluation of the Thin-layer Chromatograms of the Ni(STTA)$_2$ Chelate. The possibility of the direct quantitative determination of the $Ni(STTA)_2$ chelate, which gives the largest R_f value and a clear spot on its plate, has been investigated by measuring the intensity of its color with the photodensitometer. The spot area was determined from the curve drawn on a millimetergraph sheet after driving the densitometer across the spot. The quantitative extractions of nickel from trace amounts up to 10^{-4} M were achieved with 10^{-3} M STTA in cyclohexane in the pH region above 4.5. The calibration curve in Fig. 5 shows the relation of the areas of the spot of the $Ni(STTA)_2$ chelate developed with carbon tetrachloride *vs.* the amount initially taken. Satisfactory results could be obtained by placing, by means of a microsyringe, a sample organic solution of the STTA chelate in a definite volume of a solvent. This graphical method may be suitable for the successive determination of a few μg each of the other chelates in a developed spot.

Some Aspects of the Behavior of the STTA Chelates on the Thin-layer of Silica Gel. The R_f values of the STTA chelates with various solvents generally increase in the following order: Cd(II)<Zn(II)<Pb(II), (STTA) < Hg(II) < Co (II, III) < Cu(II) < Ni(II). This sequence differs from the acetylacetonates[2-4] the α-nitroso-β-naphtholate[5] series (Zn(II)<Co(II)<Ni(II)<Cu(II)<Co(III)), the 8-hydroxyquinolinate series[6] (Zn(II)<Cd(II)) the dithizonates series[7-12] (Cd(II)< Pb(II)< Co(II)< Zn(II)< Ni(II)< Cu(II)< Hg(II)), or the diethyldithiocarbamates series[13-17] (Co(II)<Ni(II)<Cu(II)). Acetylacetone chelates easily form their hydrate or polymerized compounds less soluble in non-polar solvents, while the STTA chelates do not form such compounds. The tailing

which usually appears in an acetylacetonate system was not observed in the STTA chelate system. It is of interest that the STTA compounds of Co(II), Ni(II), Cu(II), and Hg(II) travel a moderate distance even with such non-polar organic solvents as carbon tetrachloride and carbon disulfide. This behavior was not observed in the other chelate systems described above. It has recently been observed[24] that the replacement of oxygen by sulfur in the bis-chelate complexes of cobalt(II) and nickel(II) has two important structural consequences, the depolymerization and the stabilization of the planar form. Therefore, the depolymerization or the stabilization of the chelates, which is related to the covalency of the bond caused by the $d\pi$-$d\pi$ interaction, may become one of the important factors in these abnormal R_f trends.

24) D. H. Gerlach and R. H. Holm, *J. Amer. Chem. Soc.*, **91**, 3457 (1969).