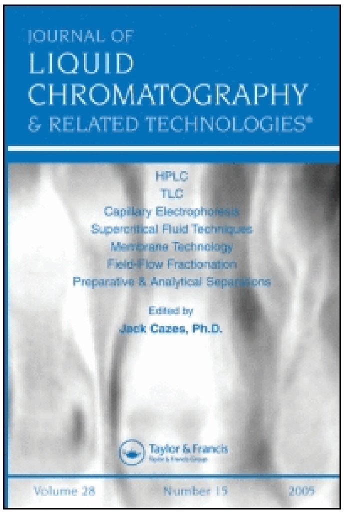

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# Thin-Layer Chromatography of Some Monothio-β-Diketonate Complexes of Nickel, Zinc and Cobalt

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# THIN-LAYER CHROMATOGRAPHY OF SOME MONOTHIO-β-DIKETONATE COMPLEXES OF NICKEL, ZINC AND COBALT

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## ABSTRACT

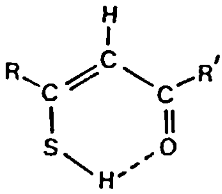
A silica gel adsorbent has been successfully used to separate three series of nickel, zinc and cobalt complexes of 1,1-difluoro-4-mercapto-4-(2'-thienyl)but-3-en-2-one, 1,1,1-trifluoro-4-mercapto-4-(2'-thienyl)but-3-en-2-one, 1,1,1-trifluoro-4-mercapto-2-(2'-naphthyl)but-3-en-2-one. For comparative purposes $R_F$ data for the protonated ligands are also included. The $ZnL_2$ complexes gave $R_F$ values in single and binary solvent systems which were similiar to the $R_F$ values of the ligands; whereas, the $NiL_2$ and $CoL_3$ complexes gave $R_F$ values which paralled each other in most solvents.

## INTRODUCTION

The thin layer chromatographic behavior of metal acetylacetonate and substituted acetylacetonate complexes on silica gel and microcrysalline cellulose has been reported.(1,2). Both

3-mercapto-1,3-diphenyl-2-propen-1-one, $C_6H_5C(SH){=}CHCOC_6H_5$, and 1,1,1-trifluoro-4-mercapto-4-(2'-thienyl)but-3-en-2-one, $C_4H_3SC(SH){=}CHCOCF_3$, have been shown to form stable and extractable chelates which can be chromatographed on a thin-layer of silica gel (3-5). Reverse-phase TLC has been applied to several metal ions spotted on a thin-layer of cellulose impregnated with the ligand, $C_4H_3SC(SH){=}CHCOCF_3$, (6). More recently a TLC separation of some of the dithio-β-diketonate complexes containing the ligand, $CH_3C(SH){=}CHCSCH_3$, has been reported (7).

We have recently noted the dipole measurements of a series of nickel, zinc and cobalt monothio-β-diketonate complexes (8). The protonated ligands include
1,1-difluoro-4-mercapto-(2'-thienyl)but-3-en-2-one,
1,1,1-trifluoro-4-mercapto-(2'-thienyl)but-3-en-2-one and
1,1,1-trifluoro-4-mercapto-(2'-naphthyl)but-3-en-2-one.



| R | R' | Ligand (LH) |
|---|---|---|
| 2'-thienyl($C_4H_3S$) | $CHF_2$ | Sthdf-H |
| 2'-thienyl($C_4H_3S$) | $CF_3$ | Sthtf-H |
| 2'-naphthyl($C_{10}H_7$) | $CF_3$ | Snptf-H |

Dipole measurements of these $NiL_2$, $ZnL_2$ and $CoL_3$ complexes support a *cis*-square planar, tetrahedral and *fac*-octahedral geometry, respectively (9-11). We have demonstrated by $^{13}C$-NMR spectroscopy that the confirmation for the $CoL_3$ complexes are indeed *fac*-octahedral (8). We now report the thin-layer chromatographic behavior of these complexes and their parent ligands on an adsorbent of silica gel.

## EXPERIMENTAL

### Plate Preparation

The commerically available thin-layer sheets (Eastment - 13179) consisted of a 100μ coating of silica gel on a poly-(ethylene terephthalate) supporting surface with polyacrylic acid as a binder. The TLC sheets were activated by heating for 30 min. at 100°C.

### Ligand and Metal Complex Preparation

The various ligands and their metal complexes were prepared as previously reported (4,5,12). They were prepared in 0.2% (W/V) chloroform.

### Solvent Systems and Detection

The solvent systems were prepared from reagent grade chemicals. The complexes were detected by their intense color and the developing time (Tables 2 and 3) was for a distance of 10 cm. The $R_F$ values are an average of four runs per sample.

## RESULTS AND DISCUSSION

The color of the ligands and their nickel, zinc and cobalt chelates are presented in Table 1. The $R_F$ values for these compounds and their ligands are displayed in Tables 2 and 3 for the

TABLE 1

Color of Ligands and Metal Complexes

| No. | Complex (Ligand) | Color | No. | Complex (Ligand) | Color | No. | Complex (Ligand) | Color |
|---|---|---|---|---|---|---|---|---|
| 1 | Sthdf-H | burgundy | 5 | Sthtf-H | red-orange | 9 | Snptf-H | red-orange |
| 2 | $Ni(thdf)_2$ | brown-green | 6 | $Ni(Sthtf)_2$ | brown-black | 10 | $Ni(Snptf)_2$ | brown |
| 3 | $Zn(thdf)_2$ | yellow | 7 | $Zn(Sthtf)_2$ | yellow | 11 | $Zn(Snptf)_2$ | yellow |
| 4 | $Co(thdf)_3$ | blue-black | 8 | $Co(Sthtf)_3$ | blue-black | 12 | $Co(Snptf)_3$ | blue-black |

TABLE 2

$R_F$ Values and Development Times of Ligands and Metal Complexes in Single Solvent Systems

| | Complex (Ligand) | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Solvent | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 3 | 9 | 10 | 11 | 12 |
| acetonitrite (27 min.) | 0.95 | 0.98 | 1.00 | 0.99 | 1.00 | 1.00 | 1.00 | 0.76 | 0.83 | 1.00 | 1.00 | 1.00 |
| nitrobenzene (105 min.) | s | 1.00 | s | 1.00 | 0.16 | 0.83 | 0.13 | 1.00 | s | 1.00 | s | 1.00 |
| benzonitrile (122 min.) | 0.48 | 0.99 | 0.29 | 1.00 | 0.27 | 0.91 | 0.32 | 1.00 | 0.38 | 0.98 | 0.40 | 0.95 |
| benzene (43 min.) | 0.45 | 0.95 | 0.22 | 0.64 | 0.09 | 0.81 | 0.05 | 0.95 | 0.07 | 1.00 | 0.13 | 0.92 |
| toluene (45 min.) | 0.48 | 0.89 | 0.24 | 0.84 | 0.11 | 0.89 | 0.09 | 0.94 | 0.18 | 0.94 | 0.10 | 0.94 |
| methylene chloride (73 min.) | 0.76 | 1.00 | s | 1.00 | 0.31 | 1.00 | 0.14 | 1.00 | s | 1.00 | s | 1.00 |
| aniline (178 min.) | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |
| anisole (69 min.) | 0.71 | 0.96 | 0.64 | 1.00 | 0.27 | 0.92 | 0.25 | 1.00 | 0.48 | 1.00 | 0.41 | 1.00 |
| chloro-benzene (57 min.) | 0.42 | 0.80 | 0.20 | 0.63 | 0.12 | 0.86 | 0.08 | 0.92 | 0.28 | 0.95 | 0.15 | 0.96 |
| xylene (54 min.) | 0.38 | 0.83 | 0.21 | 0.66 | 0.10 | 0.84 | 0.08 | 0.90 | 0.15 | 0.93 | 0.12 | 0.95 |

s - total spreading of the spot

TABLE 3
$R_F$ Values and Development Times of Ligands and Metal Complexes in Binary Solvent Systems

| | Complex (Ligand) | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Solvent | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
| 10:1 xylene-ethylacetate (46 min.) | 0.42 | 0.92 | 0.44 | 0.96 | 0.44 | 0.84 | 0.44 | 0.90 | 0.45 | 0.96 | 0.50 | 1.00 |
| 2:1 methylene chloride-chlorobenzene (54 min.) | 0.37 | 0.80 | 0.33 | 0.84 | 0.13 | 0.86 | 0.27 | 0.96 | 0.23 | 0.95 | 0.21 | 0.96 |
| 1:2 methylene chloride-chlorobenzene (68 min.) | 0.35 | 0.84 | 0.33 | 0.77 | 0.10 | 0.84 | 0.09 | 0.92 | 0.18 | 0.95 | 0.18 | 0.91 |
| 2:1 $CHCl_3$ - $CCl_4$ 104 min.) | 0.30 | 0.77 | 0.14 | 0.58 | 0.08 | 0.84 | 0.05 | 0.90 | 0.13 | 0.87 | 0.04 | 0.91 |
| 2:1 $CHCl_3$-$CS_2$ (59 min.) | 0.42 | 0.83 | 0.22 | 0.58 | 0.11 | 0.89 | 0.08 | 0.96 | 0.21 | 0.98 | 0.50 | 0.98 |
| 1:2 nitrobenzene-chlorobenzene (98 min.) | 0.50 | 0.97 | 0.50 | 0.97 | 0.14 | 0.91 | 0.12 | 1.00 | 1.00 | 1.00 | 0.50 | 1.00 |
| 1:2 cyclohexane-chloroform (93 min.) | 0.26 | 0.76 | 0.19 | 0.50 | 0.09 | 0.81 | 0.08 | 0.92 | 0.18 | 0.98 | 0.11 | 0.94 |
| 1:1 acetonitrile-benzonitrile (36 min.) | 0.78 | 1.00 | 0.81 | 1.00 | 0.69 | 1.00 | 0.78 | 1.00 | 0.78 | 1.00 | 0.82 | 1.00 |
| 1:1 benzene-acetone (49 min.) | 0.81 | 0.97 | 0.84 | 0.99 | 0.80 | 0.71 | 0.86 | 0.96 | 0.79 | 0.82 | s | 0.99 |

s - total spreading of the spot

single and binary solvents systems studied. Except for the zinc complexes which were yellow colored, the nickel, cobalt and ligand colors were much darker; however, their TLC color on silica gel was either yellow or yellow-brown. Of the single solvent systems reported only nitrobenzene and methylene chloride showed any spreading of the complexes and ligands. Within each of the three series of ligands and their Zn, Co and Ni complexes, examined, the single solvents of benzene and chlorobenzene gave good $R_F$ values. The best separations were obtained for the Sthdf-H ligand and its metal complexes. Benzenonitrile also gave reasonable separations for the Sthtf-H ligand and its metal chelates.

Better separations were obtained from the binary solvent systems. The Sthdf series gave excellent $R_F$ values in the solvents $CHCl_3$-$CCl_4$, $CHCl_3$-$CS_2$ and cyclohexane-$CHCl_3$. Similarly the Sthtf series were nicely separated in methylene chloride-chlorobenzene and in benzene-acetone solvents. The Snptf series gave a moderate separation in $CHCl_3$-$CCl_4$. The $R_F$ values of the nickel and cobalt complexes were usually larger than those of the zinc complexes and their corresponding ligands. The order of the $R_F$ values was solvent dependent, for example, in benzene: $Ni(Sthdf)_2$ > $Co(Sthtf)_2$ > Sthdf-H > $Zn(Sthdf)_2$ and in benzene-acetone: $Co(Sthtf)_2$ > $Zn(Sthtf)_2$ > Sthtf-H > $Ni(Sthtf)_2$. In general the 2'-naphthyl substituent gave higher $R_F$ values than the 2'-thienyl substituent and no trend is indicated between the trifluoromethyl and difluoromethyl substituents.

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