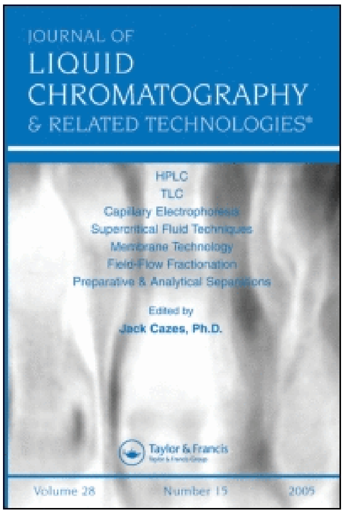

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Separation of Some Monothio-β-Diketonate Chelates by Thin-Layer Chromatography

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SEPARATION OF SOME MONOTHIO-β-DIKETONATE CHELATES BY THIN-LAYER CHROMATOGRAPHY

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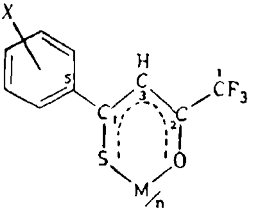
ABSTRACT

Chromatographic data of nine trifluoromonothio-β-diketonate complexes on silica gel are described. The best single or binary eluent was found to be either aromatic or contained chlorine. In a series of complexes containing the same ligand, the R_F value is related to the geometry of the complex.

INTRODUCTION

The substitution of one of the oxygen atoms with a sulfur atom in a β-diketonate ligand has been shown to yield metal monothio-β-diketonate complexes which are monomeric, anhydrous and soluble in organic solvents; whereas, metal complexes of β-diketones are solvated, polymeric and insoluble in organic solvents (1). Recently we have reported on the ^{13}C and ^{19}F NMR spectra of various trifluoro and difloromonothio-β-diketonate complexes of ligands $RC(SH)=CHCOCF_3$ and $RC(SH)=CHCOCHF_2$ (2,3) where the R substituent is aryl. In continuation of our studies on monothio-β-diketonate complexes we now report our thin-layer chromatography (TLC) results of nine metal complexes of the trifluoromonothio-β-diketonates, $RC(SH)=CHCOCF_3$, where R substituent at the thiocarbonyl carbon (see below) is $4'-C_2H_5C_6H_4$, $4'-C_2H_5OC_6H_4$, $3',5'-(CH_3O)_2C_6H_3$ and $3',4',5'-(CH_3O)_3C_6H_2$ and the metals are zinc, platinum, palladium, cobalt and nickel.



The dipole moments of metal complexes containing these four monothio-β-diketonate ligands have recently been reported (4).

A literature survey reveals that reports of several ions extracted with the ligands, 1,1,1-trifluoro-4-mercapto-4-(2'-thienyl)but-3-en-2-one and 3-mercapto-1,3-diphenyl-2-propen-1-one have been chromatographed on silica gel (5,6). Copper and iron have also been determined from the TLC of cellulose impregnated with the above mentioned ligand, $2'-C_4H_3SC(SH)=CHCOCF_3$ (7). A recent review article has summerized the analytical applications of monothio-β-diketonate complexes (8).

TABLE 1

METAL COMPLEXES OF $RC(SH)=CHCOCF_3$ (LH)

Complex (No.)	R	Color	Complex (No.)	R	Color
ZnL_2 (1)	$4'-C_2H_5C_6H_4$	yellow	NiL_2 (6)	$3',5'-(CH_3O)_2C_6H_3$	brown
ZnL_2 (2)	$4'-C_2H_5OC_6H_4$	yellow	ZnL_2 (7)	$3',4',5'-(CH_3O)_3C_6H_2$	yellow
PdL_2 (3)	$4'-C_2H_5OC_6H_4$	orange	CoL_3 (8)	$3',4',5'-(CH_3O)_3C_6H_2$	brown
PtL_2 (4)	$4'-C_2H_5OC_6H_4$	burgandy	PdL_2 (9)	$3',4',5'-(CH_3O)_3C_6H_2$	orange
CoL_3 (5)	$4'-C_2H_5OC_6H_4$	black			

EXPERIMENTAL

The TLC separations were carried out an adsorbent of silica gel (100μ) with a binder of polyacrylic acid and a supporting surface of poly-(ethylene terephthalate). The TLC sheet were activated by heating at 100°C for 30 min.

The monothio-β-diketonate chelates were prepared as previously reported (4). In Table 1 is displayed the nine complexes used and their color. Samples were prepared in 0.25% chloroform. The solvent systems were prepared from reagent grade chemicals. The spots were detected by their intense color and development time (Tables 2 and 3) was for distance of 10 cm. The R_F values given in Tables 2 and 3 are for an average of six runs per sample.

RESULTS AND DISCUSSION

In this TLC study the R_F values of nine metal complexes containing the four monothio-β-diketonate ligands were recorded in single and binary solvent systems. Table 2 shows the R_F values in a single solvent. Compounds No. 1 and 2 which differ only in the p-ethyl and p-ethoxy substituents on phenyl gave nearly the same R_F values in most solvents as did compounds No. 3. The best solvents were aromatic or contained chlorine such as chloroform, methylene chloride, benzene, xylene, nitrobenzene, chlorobenzene and benzonitrile. Chloroform, methylene chloride, and nitrobenzene gave quite different R_F values for compounds

TABLE 2

R_F DATA FOR METAL MONOTHIO-β-DIKETONATE COMPLEXES IN SINGLE SOLVENT SYSTEMS

Solvent	Complex (No.) 1	2	3	4	5	6	7	8	9	Time (min.)
methyl ethyl ketone	0.93	0.96	0.97-	0.96	0.94	0.93	0.95	0.95	0.95	45
ethyl acetate	0.97	0.97	0.97	0.98	0.93	0.91	0.95	0.97	0.93	55
carbon tetrachloride	0.06	0.00	0.39	0.39	0.19	0.16	0.00	0.00	0.00	100
chloroform	0.78	0.82	0.97	0.98	0.98	0.98	0.41	0.94	0.96	73
methylene chloride	0.41	0.41	0.92	0.96	0.97	0.94	0.07	0.23	0.64	71
benzene	0.19	0.19	0.93	0.92	0.92	0.87	0.00	0.04	0.17	67
xylene	0.15	0.13	0.83	0.84	0.81	0.66	0.00	0.00	0.06	46
nitrobenzene	0.48	0.56	1.00	1.00	1.00	0.99	0.14	0.49	0.70	105
chlorobenzene	0.14	0.14	0.86	0.87	0.83	0.68	0.00	0.00	0.05	54
benzonitrile	0.48	0.48	1.00	1.00	1.00	0.86	0.26	0.80	0.88	67

TABLE 3

R_F DATA FOR MONOTHIO-βDIKETONATE COMPLEXES IN BINARY SOLVENT SYSTEMS

Solvent	Complex (No.)									Time (min.)
	1	2	3	4	5	6	7	8	9	
methylethyl ketone n-hexane(1:1)	0.79	0.79	1.00	1.00	0.97	0.69	0.41	0.97	0.94	55
methylethylketone-cyclohexane (1:1)	0.81	0.82	1.00	1.00	0.97	0.71	0.41	0.93	0.92	58
cyclohexane-chloroform (1:1)	0.14	0.22	0.82	0.83	0.57	0.53	0.00	0.00	0.06	87
chloroform carbon disulfide (1:1)	0.16	0.14	0.90	0.91	0.74	0.71	0.00	0.00	0.09	55
chloroform-CCl_4 (1:1)	0.16	0.14	0.91	0.95	0.92	0.89	0.00	0.03	0.15	94
benzene-acetone (1:1)	0.82	0.81	0.96	0.97	0.98	0.80	0.76	0.96	0.95	49

methylene chloride-chlorobenzene (1:1)	0.19	0.31	0.95	0.92	0.88	0.87	0.01	0.06	0.23	66
nitrobenzene chlorobenzene	0.48	0.55	1.00	1.00	1.00	0.97	0.00	0.29	0.60	161
CCl_4-chloroform (2:1)	0.25	0.21	0.91	0.93	0.84	0.79	0.00	0.03	0.12	108
xylene-ethylacetate (2:1)	0.50	0.48	0.96	0.95	0.96	0.94	0.67	0.81	0.86	43
xylene-ethylacetate (5:1)	0.50	0.50	0.98	0.96	0.87	0.91	0.31	0.58	0.81	45
xylene-ethylacetate (10:1)	0.50	0.50	0.96	0.96	0.94	0.82	0.22	0.47	0.64	47
chloroform-cyclohexane (2:1)	0.23	0.14	0.85	0.83	0.77	0.73	0.00	0.03	0.14	98
methylene chloride-chlorobenzene (2:1)	0.21	0.20	0.94	0.95	0.95	0.85	0.00	0.09	0.25	49
nitrobenzene-chloroform (1:2)	0.23	0.25	1.00	1.00	1.00	0.93	0.00	0.17	0.41	69

No. 7, 8 and 9. While the ligand is the same, 3', 4' 5'-$(CH_3O)_3C_6H_2C(SH)=CHCOCF_3$, in these complexes the R_F value is probably related to the geometry of the complex which is tetrahedral, *fac*-octahedral and *cis*-square planar, respectively (2,4). Except for zinc complexes which were yellow in color, the other complexes were more intense in color in the solid state and in solution; however, their TLC color on silica gel was either yellow or an orange, brown or green shade of yellow.

The binary solvents shown in Table 3 also gave a range of R_F values when a chlorine containing solvent was used. The methylene chloride-chlorobenzene (1:1) solvent gave the more diverse range of R_F values. Changing this solvent ratio to 1:2 or 2:1 did not give R_F values with a larger spread as 1:1 solvent ratio. Changing the composition of the xylene-ethylacetate solvents had only a small effect on the R_F value of all the complexes except No. 7, 8 and 9 where an increase in xylene concentration lowered the respective R_F value for each complex. Of the three zinc complexes (No. 1, 2, 7), compound No. 7 gave the smallest R_F value in most solvents as compared to complexes No. 1 and 2. Similarily the cobalt complexes (No. 5 and 8) and the palladium complexes (No. 3 and 9) also show the smaller R_F values when the ligand is 3', 4', 5'-$(CH_3O)_3C_6H_2C(SH)=CHCOCF_3$. It is also interesting to note that of a series of complexes containing the same ligand (No. 2, 3, 4, 5 and also No. 7, 8, 9) the tetrahedral ZnL_2 complexes have the lower R_F values (No. 2 also No. 7). It would seem that in the solvents studied increased aryl substitution as well as a tetrahedral geometry favor a lower R_F value. Finally for the complexes of *cis*-square planar geometry (No. 3, 4, 6, 9) increased aryl substitution (No. 9) has a greater effect on the R_F value (lower) than the metal complexed.

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