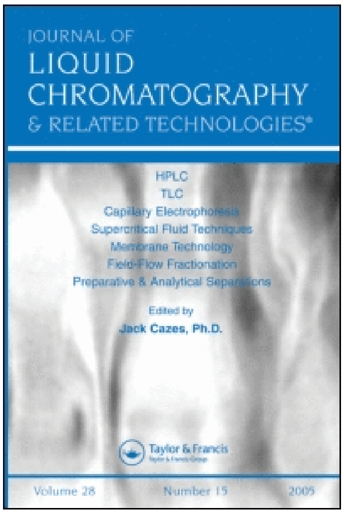

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NORMAL AND REVERSED PHASE THIN-LAYER CHROMATOGRAPHY OF TRANSITION METAL COMPLEXES OF MONOTHIO-β-DIKETONES

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ABSTRACT

Various groupings from eighty-two metal complexes of monothio-beta-diketones having different ligands, have been studied by normal and reversed phase thin-layer chromatography in single and binary solvent systems. The data is discussed in terms of keeping the ligand, RCSCHCOR′, constant and varing the metal; keeping the metal constant and varying the R′-group of the ligand; keeping the metal constant and varying the R-group of the ligand.

Separation patterns are discussed in terms of choice of solvent systems and the magnitude of the R_f values are discussed with reference to the R and R′-groups of the ligand.

INTRODUCTION

Monothio-β-diketonate complexes are monomeric, anhydrous and soluble in organic solvents, whereas, metal complexes of β-diketones are solvated and insoluble in organic solvents (1). The thin-layer chromatographic behavior of some metal β-diketonates on silica gel and microcrystalline cellulose has been reported (2,3). Stable and extractable chelates of two monthio-β-diketones, RCSCHCOR′, where R and R′ are phenyl and R is 2′-thienyl and R′ is trifluoromethyl has been done (4-6). Also a TLC separation of some dithio-β-diketonate complexes has been reported (7). More recently we have used a silica gel adsorbent to separate some trifluoro-β-diketonate complexes (8) and to separate three series of nickel, zinc and cobalt complexes with the ligands having R-2′-thienyl, R′-CHF_2; R-2′-thienyl, R′-CF_3; R-2′-naphthyl, R′-CF_3 (9).

We now report the thin-layer chromotographic behavior of eighty-two metal complexes of monthio-β-diketones using normal and reversed phase TLC in single and binary solvent systems.

EXPERIMENTAL

Plate Preparation

Normal phase TLC was done on silica gel (100μ) sheets (Eastman) on a flexible polyethylene terephthalate suporting surface with a polyacrylic acid as a binder. The TLC sheets were activated by heating at 100°C for 1 hr. Reversed phase TLC was done on KC_{18} plates (Whatman).

Solvent Systems and Detection

Eleven single solvent (Table 1), fourteen binary solvent (Table 2) and six reversed phase solvent (Table 3) systems were used in the separation studies. The intense color of the complexes in most cases was used for detection. The Cu and some

Table 1 Single Solvents

System No.	Solvent	System No.	Solvent
1	CH_3CN	7	$C_6H_4(CH_3)_2$
2	$C_6H_5NO_2$	8	$C_6H_4(CH_3)_2$
3	CH_2Cl_2	9	C_6H_6
4	$C_4H_8O_2$	10	CCl_4
5	C_6H_5Cl	11	CS_2
6	$CHCl_3$		

Table 2 Binary Solvents

System No.	Binary Solvents	System No.	Binary Solvents
12	$CH_3CN:CCl_4$ (3:7)	19	$CCl_4:C_6H_5Cl$ (1:4)
13	$CH_2Cl_2:C_6H_5Cl$ (2:1)	20	$C_6H_4(CH_3)_2:C_4H_8O_2$ (9:1)
14	$CH_2Cl_2:CCl_4$ (1:1)	21	$C_6H_4(CH_3)_2:C_4H_8O_2$ (10:1)
15	$CHCl_3:CCl_4$ (2:1)	22	$CHCl_3:CS_2$ (1:2)
16	$C_6H_{12}:C_4H_8O_2$(2:1)	23	$CH_2Cl_2:CS_2$ (1:9)
17	$CH_2Cl_2:CS_2$ (1:4)	24	$CS_2:C_4H_8O_2$ (9:1)
18	$CHCl_3:CS_2$ (1:1)	25	$C_6H_6:CCl_4$ (3:7)

Table 3 Reversed Phase Solvents

Solvent System	Solvent	Solvent System	Solvent
1	95% ethanol	4	n-pentanol
2	n-propanol	5	3-methyl-1-butanol
3	n-butanol	6	t-butyl alcohol

Zn chelates were void of color but they were visible under UV light. For some of the Zn, Ni and Pd chelates the color faded and a dilute solution of dithizone in 6 M NH_3 when sprayed on these chelates gave the following colors: pink (Zn), blue (Ni), orange (Pd). The developing time was for a 10 cm distance with R_f values held to a reproducibility of 0.03 R_f units, with a good separation having the R_f values differ by at least 0.05 R_f units.

RESULTS AND DISCUSSION

The various complexes studied are presented in Table 4. The four-coordinate Ni, Pd and Pt complexes are cis-square planar and the six-coordinate Co, Zn, Fe, Ru and Ru complexes are facial (cis) octahedral. The geometry of the four-coordinate Cu complex is not known. The four-coordinate Zn complex is tetrahedral. The R_f data was analyzed for three basic patterns: ligand constant-vary the metal; R of the ligand constant - vary R´ of the ligand; keeping R of the ligand constant and vary R´

Table 4 Substituted Monothio-β-diketonate Chelates

Series	R	R′	Metal
1	CH_3	CF_3	Ni, Zn, Co
2	CH_3	C_6H_5	Ni, Pd, Zn, Co, Fe
3	C_2H_5	CF_3	Ni, Zn, Co
4	$(CH_3)_2CHCH_2$	CF_3	Ni, Pd
5	C_6H_5	OC_2H_5	Ni, Pd, Zn, Co
6	C_6H_5	C_6H_5	Ni, Pd, Zn, Co, Rh
7	p-$CH_3C_6H_4$	C_6H_5	Ni, Pd, Zn, Co, Fe
8	C_6H_5	CF_3	Ni, Pd, Pt, Zn, Cu, Co, Rh, Ru
9	C_6H_5	C_2F_5	Ni, Pd, Co
10	C_6H_5	C_3F_7	Ni, Pd, Co
11	p-FC_6H_4	CF_3	Pd, Pt, Rh, Ru
12	p-$CH_3C_6H_4$	CF_3	Ni, Pd, Pt, Zn, Cu, Co, Rh, Ru
13	2′-$C_{10}H_7$	CF_3	Ni, Pd, Pt, Co, Rh, Ru
14	2′-$C_{10}H_7$	C_2F_5	Ni, Pd, Co
15	2′-$C_{10}H_7$	C_3F_7	Ni, Pd, Co
16	2′-C_4H_3S	CHF_2	Rh, Ru
17	2′-C_4H_3S	CF_3	Ni, Pd, Pt, Cu, Co, Rh, Ru, Fe
18	2′-C_4H_3S	C_2F_5	Ni, Pd, Co
19	2′-C_4H_3S	C_3F_7	Ni, Pd, Co
20	2′-$CH_3C_4H_2S$	CF_3	Rh

of the ligand. R and R´ refer to the ligand´s substituents of RCOCHCSR´.

SINGLE SOLVENT SYSTEMS

a. Ligand Constant/Vary the Metal

Table 5 displays mixtures of the monthio-β-diketonates which are separable by 0.05 R_f units. The data suggests that the nonpolar solvents of carbon disulfide and carbon tetrachloride are excellent solvent choices. In general these two solvents gave low R_f values. The polar solvents of acetonitrile, nitrobenzene and methylene chloride gave the expected high R_f values. Separations in most of these solvents proved to be poor choices as the chelate moved with the solvent front. Ethyl acetate gave varying R_f values and in some mixtures gave good separations. Benzene, with its low dielectric constant, was expected to give low R_f values; however, the reverse situation was found and therefore benzene has limited ability for separation. Toluene generally gave lower R_f values than benzene, but also proved to be of limited use in separations. Chloroform, mixed xylenes and chlorobenzene gave R_f values of intermediate value in the 10 cm. range and showed potential as developing solvents for certain mixtures. Acetonitrile resulted in the streaking of some chelates. Methylene chloride and toluene produced tailing in the nickel and cobalt chelates.

Several observations with regard to the metal can be made from Table 5. Nickel and palladium chelates are often not

Table 5 R_f Value Trends - Single Solvent Systems

Ligand	Trend	Solvent
$CH_3CSCH_2COCF_3$	Zn < Co < Ni	11
$CH_3CSCH_2COC_6H_5$	Co,Fe < Zn < Pd,Ni	11
$C_2H_5CSCH_2COCF_3$	ZN < Co < Ni	11
	Zn < Ni < Co	4
$C_6H_5CSCH_2COOC_2H_5$	Zn < Co < Ni,Pd	11
$C_6H_5CSCH_2COC_6H_5$	Co < Rh < Ni,Pd < Zn	11
	Zn,Co < Ni,Pd < Rh	2,3,5
$C_6H_5CSCH_2COCF_3$	Zn < Ni,Cu,Co < Rh < Pt,Pd,Ru	3,4,8
	Zn < Cu,Co < Ru < Ni < Rh < Pd,Pt	11
$C_6H_5CSCH_2COC_2F_5$	Co < Ni < Pd	11
	Ni < Co,Pd	4,5,6
$p\text{-}FC_6H_4CSCH_2COCF_3$	Ru < Pd < Pt < Rh	11
	Rh < Pd,Pt,Ru	5,8,10
$p\text{-}CH_3C_6H_4CSCH_2COCF_3$	Zn < Cu,Co < Ru < Rh,Ni < Pd,Pt	11
	Zn < Cu < Co < Rh < Ni < Ru < Pd,Pt	10
$2'\text{-}C_{10}H_7CSCH_2COCF_3$	Co < Ru < Ni < Pd,Pt < Rh	11
	Co < Ni < Pd < Rh < Ru < Pt	10
$2'\text{-}C_{10}H_7CSCH_2COC_2F_5$	Co < Ni < Pd	11
$2'\text{-}C_{10}H_7CSCH_2COC_3F_7$	Ni < Pd,Co	11,6,4
$2'\text{-}C_4H_3SCSCH_2COCHF_2$	Rh < Ru	1,5,6,7,8
$2'\text{-}C_4H_3SCSCH_2COCF_3$	Fe < Cu,Ru,Co,Ni < Pd,Pt,Rh	11
$2'\text{-}C_4H_3SCSCH_2COC_2F_5$	Ni < Co < Pd	11
$2'\text{-}C_4H_3SCSCH_2COC_3F_7$	Ni < Co < Pd	11

separable as were the chelates of palladium and platinum. However, nickel can be separated from either palladium or platinum. Cobalt and zinc can be separated from each other as well as from all other metals containing various ligands. Cobalt, iron, ruthenium and rhodium are separable as a mixture. Copper can be separated from both square planar complexes as well as octahedral complexes. In general in a mixture containing a larger number of metals, separation and identification would be limited to approximetaly four to six metal chelates depending on the ligand used, due to production of similar R_f values with these single solvent systems.

The R_f values from single solvent development reflect certain trends between the transition metals investigated. Overall, the nickel and palladium complexes give R_f values greater than the corresponding cobalt and zinc complexes. For only nickel and palladium complexes, the latter yields larger R_f values. Ruthenium complexes yields greater R_f values than rhodium complexes while both gave greater R_f values than cobalt complexes. Iron, zinc and copper complexes yield very low R_f values. It is important to notice that the chelates of certain ligands do not yield specific trends. In these cases, the R_f values show much scatter.

b. R Constant/Vary R´

In analyzing the substituent effects of the monothio-β-diketone metal chelates on the R_f values by holding the R substituent constant and varying the R´ substituent, the data follows along two lines. First, the R substituent can be either electron rich or electron poor in nature. Second, the R´ substituent can be changed from one which is electron rich to electron poor. Also when the electron withdrawing substituent is a perfluoroalkyl group, the R_f values can be studied by varying the length of the carbon chain.

Keeping the R substituent as methyl and varying the R´ substituent methyl group to a phenyl group, the R_f values failed to show a consistent trend between the chelates on zinc, nickel and cobalt for single solvent systems. For the nickel and cobalt chelates only, the order of R_f values is $C_6H_5 < CH_3$, and the pattern for the zinc chelate is the reverse order.

In the case of the electron rich R-group, the R´ substituent was varied as: OC_2H_5, C_6H_5, CF_3, C_2F_5 and C_3F_7 for chelates of nickel, palladium and cobalt. In changing the R´ substituent from OC_2H_5 to C_6H_5 or in changing from either OC_2H_5, C_6H_5 to CF_3, the metal chelates fail to show a trend in R_f values for these single solvent systems. However, when the R´ substituent is a perfluoroalkyl group, a pronounced effect on the R_f values is seen as the length of the carbon chain is increased. With the nonpolar and nonaromatic solvents, carbon disulfide and carbon tetrachloride, the following trend is observed; $CF_3 < C_2F_5 < C_3F_7$.

This order of the R_F values remains the same when R is naphthyl for the aromatic solvents of xylene and chlorobenzene; however, the trend changes from $CF_3 < C_3F_7 < C_2F_5$ in the previously mentioned solvents. When the electron rich substituent (R) is thienyl, the R_f values follow the first trend for the solvent carbon disulfide. This same trend is observed for the corresponding palladium series in a nitrobenzene or chlorobenzene solvent and the latter trend is observed in the solvent carbon disulfide. The ruthenium and rhodium series in which the R substituent is thienyl the order of R_f values for the complete range of single solvent systems $CHF_2 < CF_3$.

c. Vary R/R´ Constant

The R´ substituents used for this study are C_6H_5, CF_3, C_2F_5 and C_3F_7. As in the previous section, the variable substituent is changed from one which is electron rich to one which is electron poor. For electron poor substituents, the effect of increasing the length and substitution of the alkyl chain on the R_f values was done. If the R substituent is a phenyl group, the effect of substituting the phenyl ring on the R_f values was also studied.

For the nickel and palladium series and in which the R´ substituent is phenyl the R substituent is changed from CH_3 to C_6H_5, the pattern of R_f values is such that $C_6H_5 < CH_3$ when carbon disulfide is the developing solvent. The reverse trend is found for the corresponding zinc and cobalt series and these trends are also followed for some chlorinated and aromatic solvents.

When the R′ substituent is a perfluromethyl group and the R substituent is an alkyl group, a consistent trend is observed in each series of the nickel, palladium and zinc chelates. As the length and substitution of the alkyl chain is increased, the R_f values increase. In the case of the nickel and palladium chelates on changing from a alkyl substituent to a phenyl substituent, there is a corresponding decrease in R_f values. No consistent trend in this regard is seen for the zinc chelates. In aromatic solvents, chlorobenzene and xylene, as the substitution of the phenyl (R) substituent is varied and R′ is CF_3 the R_f values increase for $FC_6H_4 < CH_3C_6H_4 < C_6H_5$. The trend observed is reversed for the nonpolar solvents of carbon disulfide and carbon tetrachloride.

For the substituents, C_6H_5, $2'$-$C_{10}H_7$ and $2'$-C_4H_3S, the following pattern is observed for the palladium series in both carbon disulfide and carbon tetrachloride and also the platinum series in carbon disulfide, $C_{10}H_7 < C_4H_3S < C_6H_5$. However, this order changes for the platinum series when the developing solvent is carbon tetrachloride. The observed trend is, $C_4H_3S < C_{10}H_7 < C_6H_5$. This new pattern also follows for the corresponding ruthenium and rhodium series when the developing solvent is either carbon disulfide or carbon tetrachloride. The rhodium series expands the pattern as follows, $CH_3C_4H_3S < C_4H_3S < C_{10}H_7 < C_6H_5$.

Using copper chelates, two substituents, C_6H_5 and C_4H_3S were compared and the results correspond to the other metals when the developing solvents are carbon disulfide and carbon tetrachloride. For these chelates, the R_f values are, $C_4H_3S < C_6H_5$.

The pattern in R_f values just described is reversed when the R´ substituent is changed to a perfluroroethyl group. For the nickel, palladium and cobalt series, the pattern changes to, $C_6H_5 < C_{10}H_7$. The R_f values of the thienyl substituted chelates fluctuates and thus does not fit into a consistent trend. The expected trend was the opposite of that which was observed.

Two different patterns exist when the R´ substituent is a perfluroropropyl group as the R substituent is varied from C_6H_5, to $C_{10}H_7$ to C_4H_3S. The nickel series follows the trend seen when the R´ substituent is CF_3. However, the trend breaks down to $C_{10}H_7$, $C_4H_3S < C_6H_5$, for cobalt and palladium chelates.

2. BINARY SOLVENT SYSTEMS

a. Ligand Constant/Vary the Metal

The use of binary solvent systems allows the separation of certain mixtures that were not possible in single solvent systems. In general, nonaromatic solvent systems provided the best separations. Solvent system No. 23 proved to be one of the best combinations. This was not unexpected as the major component is carbon disulfide. For most successful solvent systems at least one of the components was chlorinated. Table 6 lists the separation trends that were observed using binary solvent systems having R_f values that differ at least by 0.05 units.

Using binary solvent systems, palladium and nickel could be easily separated. However, as in the single solvent systems, the platinum and palladium complexes could not be separated. Zinc chelates again can be separated from any other metal. Ruthenium and rhodium are also separable. Unlike the single solvent systems, cobalt, ruthenium, rhodium and iron complexes are not always separable. The copper chelates of certain ligands gave R_f values of similiar magnitude to the corresponding cobalt and iron chelates.

The zinc, copper and iron chelates again yield the lowest R_f values in the separation of most mixtures. From Table 6 the difference in trends between single and binary solvent systems occurs in ligands in which the R substituent is electron rich in nature. For example the ligand, $C_{10}H_7CSCH_2COC_2F_5$, the following pattern is observed for three metal chelates using carbon disulfide as the developing solvent; Co < Ni < Pd. However, when the developing solvent is changed to $CHCl_3$:CS_2 (1:1), the pattern is rearranged to Ni < Co < Pd. Within mixtures of four or more complexes trends are not obvious. The nickel chelates in binary solvents generally have lower R_f values than the corresponding

Table 6 R_f Value Trends - Binary Solvent Systems

Ligand	Trends	Binary Solvent Systems
$CH_3CSCH_2COCF_3$	Zn < Co < Ni Zn < Ni < Co	17, 22, 23 14, 15, 19
$CH_3CSCH_2COC_6H_5$	Co < Fe < Pd,Ni < Zn Fe < Co < Zn < Ni,Pd	13, 23 17, 18, 22
$(CH_3)_2CHCH_2CSCH_2COCF_3$	Ni < Pd	12, 15, 16, 17, 23
$C_2H_5CSCH_2COCF_3$.	Zn < Ni < Co Zn < Co < Ni	14, 19 15, 17, 23
$C_6H_5CSCH_2COOC_2H_5$	Zn < Co < Ni,Pd	13, 14, 17, 19, 23, 25
$C_6H_5CSCH_2COC_6H_5$	Pd < Ni < Co < Rh < Zn	23, 25
$C_6H_5CSCH_2COCF_3$	Zn < Co,Cu < Ru < Ni,Pd,Pt,Rh	23
$C_6H_5CSCH_2COC_2F_5$	Ni < Pd,Co	12, 14, 16, 21, 23
$C_6H_5CSCH_2COC_3F_7$	Ni < Co < Pd	16, 20
p-$CH_3C_6H_4CSCH_2COCF_3$	Zn < Cu,Co,Ru,Rh,Ni,Pd,Pt	12, 13, 14, 15, 16
2′-$C_{10}H_7CSCH_2COCF_3$	Rh < Ru < Pt,Pd Rh < Ru,Pt,Pd	22, 23 12, 15, 19, 25
2′-$C_{10}H_7CSCH_2COC_2F_5$	Pt < Ni < Pd Ni < Co << Pd	16, 19, 20, 24 13, 14, 16, 18, 19, 20, 22
2′-$C_{10}H_7CSCH_2COC_3F_7$	Ni < Co < Pd	14, 16, 24
2′-$C_4H_3SCSCH_2COCHF_2$	Ru < Rh Rh < Ru	14, 19, 21 15, 18, 22, 25
2′-$C_4H_3SCSCH_2COC_2F_5$	Ni < Co < Pd	14, 16, 19, 20, 21, 22, 24
2′-$C_4H_3SCSCH_2COC_3F_7$	Ni < Co < Pd	15, 16, 19, 20, 21, 23, 24

cobalt chelates. This also is the opposite of what was observed with single solvent systems.

b. R Constant/Vary R′

The use of binary solvent systems yields several trends in the R_f values as the R substituent is held constant and the R′ substituent is varied. The R substituent in each case is electron releasing, while the R´ substituent varies from electron releasing to electron withdrawing. A series of zinc chelates having the electron releasing R as CH_3 gave a pattern of R_f values which was the reverse order for the corresponding nickel and cobalt chelates when the R´ substituent was changed from a phenyl group to a trifluoromethyl group. This R_f pattern of $C_6H_5 < CF_3$ suggests that as you increase the electron withdrawing capabilities of the R´ substituent, the R_f values also increase. This pattern was not observed in single solvent systems.

Other R electron rich substituents of C_6H_5 and C_4H_3S show a definite pattern in R_f values as R´ is varied for nickel, palladium and cobalt. However, if the R substituent is the larger 2´-$C_{10}H_7$, only a scatter of R_f values can be recorded for the corresponding series. When the R substituent is a phenyl group and the R´ substituent is changed from C_6H_5 to CF_3, opposite effects on the R_f values are noticed for the zinc and cobalt series. The cobalt and palladium series show the R_f values to decrease when the R´ substituent is changed from CF_3 to C_6H_5. The zinc and nickel series show the R_f values to increase as the electron releasing strength of the substituent is increased. However in the zinc series, the R_f values decrease when the electron releasing strength of the R´ substituent is changed to an alkyl group. Therefore, in these systems, the R_f values fail to yield a trend of order as the electron releasing or electron withdrawing power of the substituent is varied. Further with the zinc chelates, the opposite trend in R_f values for the R′ substituents of CF_3 and C_6H_5 occur when the R substituent is changed from electron releasing to electron withdrawing.

For the nickel, palladium and cobalt series in which the R substituent is a phenyl group, a common pattern in the R_f values occurs for binary solvent systems as the R′ substituent is changed from OC_2H_5 to C_6H_5. The trend being; $C_6H_5 < OC_2H_5$. This trend is consistent for a wide range of polarity and chemical composition of the solvent. This trend again indicates that the R_f values increase as the electron withdrawing capability is increased.

For perfluoroalkyl substituents, the trend in R_f values is similiar to that seen with single solvent systems when the R substituent is C_6H_5 or C_4H_3S. In these cases, the trend in R_f values for most binary solvent systems is such that; $CF_3 < C_2F_5 < C_3F_7$. However, when the R substituent is the larger $2'$-$C_{10}H_7$ group, no trend is observed.

This trend is expanded to $CHF_2 < CF_3 < C_2F_5 < C_3F_7$ for ruthenium and rhodium chelates when the R substituent is thienyl and the R′ substituent is varied from CF_3 to CHF_2. Therefore when the R substituent is electron rich, the R_f values increase as the R′ substituent′s electron withdrawing ability is also increased.

c. Vary R/R´ Constant

A consistent pattern for the metal chelate series of nickel, cobalt, ruthenium, rhodium, copper and palladium is observed when the R´ substituent is maintained as a fluorinated alkyl group and the R substituent is varied as C_4H_3S, $CH_3C_6H_4$, C_6H_5 and $C_{10}H_7$. The pattern in R_f values is $C_4H_3S < CH_3C_6H_4$, C_6H_5, $C_{10}H_7$ when the R´ substituent is CF_3. This pattern again suggests that as the electron withdrawing ability is increased, the R_f values likewise increase. The order, $C_{10}H_7 < C_6H_5$, is followed for the platinum, ruthenium and rhodium series. The reverse order is found for the corresponding palladium series. The former trend is also observed for the nickel, palladium and cobalt series when the R´ substituent is either C_2F_5 or C_3F_7. The zinc series does not support the correlation between the magnitude of R_f values and the electron withdrawing ability of the substituent as is evident by the following trend, $C_6H_5 < CH_3C_6H_4 < CH_3$.

In several series, the effect of placing a substituent on the phenyl R group was observed. According to the order of substituent ability, the R_f values should increase as follows, $CH_3C_6H_4 < C_{10}H_7 < C_6H_5 < FC_6H_4$. This order is not strictly followed in any series. In most series, the phenyl substituted chelate has the largest R_f value.

The results do not reveal any definite patterns in the R_f values of the different chelate series investigated for the effects of alkyl substituents in the R position. For example, in the nickel and cobalt series as the length and substitution of the alkyl substituent is increased, the R_f values should also increase. Instead they show much scatter in these binary solvent systems. Also, in the zinc series, the opposite trend from the expected one is found. In this series, the R_f values decrease as the electron withdrawing ability is increased when the R substituent is changed from CH_3 to C_2H_5.

In considering the effect of changing the R substituent from an alkyl to a phenyl group when the R′ substituent is a fluorinated alkyl group, the R_f values show that for the majority of the binary solvent systems, $C_6H_5 < CH_3$. This was observed in all nickel, cobalt, palladium and zinc series and also with single solvent systems. However when the R′ substituent is phenyl, the R_f values show much scatter for these series of metal chelates.

3. REVERSED PHASE TLC

The cobalt nickel, copper and zinc chelate of series 7 (Table 4), the cobalt, nickel and palladium chelates of series 13 and the cobalt, nickel and palladium chelates of series 14 are separable in $(CH_3)_3COH$, C_2H_5OH (also $C_5H_{11}OH$) and C_2H_5OH, respectively. In most alcohols, the platinum and palladium chelates gave nearly identical R_f values. Also these d^8-metal chelates gave lower R_f values than the octahedral chelates, except for the six-coordinate iron complex in series 7 where the

R_f values are Fe < Ni, Pd < Co < Zn in C_2H_5OH. Octahedral chelates can be separated from each other in more alcohol solvent systems than can the corresponding square planar complexes. A tetrahedral complex can always be separated from either a square planar or octahedral complex. For the eight chelates having R-C_6H_5 and R′-CF_3 of the ligand, the following trend of R_f values was observed: Pd, Pt < Ni < Ru, Rh < Co < Cu < Zn. Thus, there appears to be a dependence on geometry and R_f values for a mixture of chelates when using alcohol solvent systems in reversed phase thin-layer chromatography.

CONCLUSIONS

It is difficult to separate large mixtures of four or more metal ions with substituted monothio-β-diketones by 0.05 R_f units either single or binary solvent systems with normal phase thin-layer chromatography. Separation of 0 03 R_f units or less are easily achieved in either solvent system. For single solvent systems, the nonpolar solvents of carbon disulfide and carbon tetrachloride offer the most potential as developing solvent. Chloroform, xylenes and chlorobenzene also offer some potential. In binary solvent systems, those systems in which the major component is carbon disulfide are excellent solvents for separation. The magnitude of the R_f values is not dependent on the polarity of the solvent systems.

The ability to separate two metals is mainly dependent on the choice of ligand. Therefore, it is possible to separate any two metals by choosing the proper ligand. For some ligands, it is difficult to separate those metals which form chelates of like geometry, whereas, using these same ligands, metals from the same period in the periodic table can be separated and identified. The trends in R_f values do not show a dependence in geometry in either single or binary solvent systems. Binary systems do not necessarily offer better separations. Reversed phase thin-layer chromatography offers more sensitivity and therefore a greater ability to separate these mixtures.

Two important patterns in the magnitude of the R_f values are found as one substituent is held constant while the electron releasing and electron withdrawing ability of the other substituent is varied. First, when the R substituent is an electron releasing group, the R_f values increase as the electron withdrawing power of the R′ substituent is increased. The second pattern involve holding the R′ substituent constant as a perfluoroalkyl group and changing the R substituent. In the second pattern, a trend of increasing R_f values as the electron withdrawing ability of the R substituent is increased is followed for thienyl and phenyl substituents. This trend is broken when considering a group of large substituents: C_6H_5, $CH_3C_6H_4$ and FC_6H_4. The trend of the first pattern implies that with increasing the electron withdrawing ability of the R′ substituent, the chelate become a more polar complex. Due to the lack of consistency when the R substituent is varied, it is implied that the more significant changes occur when the R´ substituent is varied. Changing of the R´ substituent offers more potential for the manipulation of the R_f values.

Reversed phase thin-layer chromatography is more sensitive in its ability to separate the transition metal chelates of substituted monothio-β-diketones. In general, as the length of a straight chain primary alcohol increases (Table 3), the R_f value increases then decreases as the solvent is changed to a branched alcohol.

REFERENCES

1. Cox, M. and Darken, J., Metal Complexes of Thio-β-Diketones, Coor. Chem. Rev., 7, 29 (1971). See also Mehrotra, R.C., Bohra, R. and Gaur, D.P. Metal β-Diketones and Allied Derivatives, Academic Press, New York, 1978, Chp. 5,6.

2. Saitoh, K. and Suzuki, N., Thin-Layer Chromatography of β-Diketones and Their Metal Chelates, J. Chromatogr., 92, 371 (1974).

3. Haworth, D.T. and Hung, Y. Separation of Acetylacetonate Chelates by Thin-Layer Chromatography, J. Chromatogr., 201, 108 (1975).

4. Honjo, T. and Kiba, T., 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 Cadmiun (II) as Their STTA Complexes by Thin-Layer Chromatography on Silica Gel, Bull. Chem. Soc. Japan, 46, 3768 (1973).

5. Honjo, T., Honnami, H. and Kiba, T., The Separation of Iron (III), Cobalt (II), Nickel (II), Copper (II), Zinc (II), Mercury (II), Lead (II), Cadmium (II) and Palladium (II) as their SDBM Complexes by Thin-Layer Chromatography on Silica Gel, Bull. Chem. Soc. Japan, 51, 1559 (1978).

6. Maller, H. and Rother, R. Separation and Photometric Determination of Some Transition Metals as Monothio-β-diketonates by Thin-Layer Chromatography, Anal. Chim. Acta, 66, 49 (1973).

7. Honjo, H. and Otaki, T., Separation of Metal Chelates with Dithioacetylacetone by Thin-Layer Chromatography, Z. Anal. Chem., 300, 413 (1980).

8. Haworth, D.T., Mass, D.L. and Das, M., Separation of Some Monthio-β-Diketonate Chelates by Thin-Layer Chromatography, J. Liq. Chromatogr., 4, 897 (1981).

9. Haworth, D.T., Maas, D.L. and Das, M., Thin-Layer Chromatography of Some Monthio-β-Diketonate Complexes of Nickel, Zinc and Cobalt, J. Liq. Chromatogr., 4, 907 (1981).