

Linkage Between Separation of Cu^{2+} , Co^{2+} , and Ni^{2+} on TLC and Crystal Field Theory

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Abstract

$\text{M}(\text{DEDTC})_2$ ($\text{M} = \text{Cu}, \text{Co}, \text{or Ni}$) and $\text{M}(\text{PyDTC})_2$ ($\text{M} = \text{Cu or Co}$) complexes prepared by reactions of sodium diethyldithiocarbamate (NaDEDTC) and ammonium pyrrolidinedithiocarbamate (NH_4PyDTC) with metal (II) nitrates are examined for qualitative analysis and separation using thin-layer chromatography (TLC) systems in the literature. Already known separability of metal cations cited and their complexes are reexamined and discussed in the context of relation to the crystal field theory (CFT) and TLC as a new approach and adaptation. Because the chromatographic data have been agreed on with assumptions of CFT, it is concluded that CFT is closely related to the TLC separation of these metal cations and their complexes. Therefore, this study may be useful in understanding of the linkage between the CFT on coordination chemistry and the chromatographic parameters [e.g., retention factor (R_f) and theoretical plate numbers (N)] of the complexes.

Introduction

The crystal field theory (CFT) is one of three main theories used to explain macroscopic and microscopic properties of transition metal complexes, such as color, hydration energy, crystal lattice energy, hydrated radius, redox potential and electronic spectra (1–3), ion exchange on cation exchanger (4), and solvent extraction (1) part of coordination chemistry. Two other theories are valence bond theory (VBT) and molecular orbital theory (MOT) (2,3).

CFT assumes that the interaction of the d orbitals of the central atom with ligands is essentially electrostatic, and the bond between metal atom and ligands is totally ionic. In addition, the degenerated d orbitals of transition metal is separated to two group as e_g and t_{2g} under effect of negatively charged ligands approaching along with various spatial directions. Complexes are stabilized or destabilized depending on electron or electrons are present at e_g or t_{2g} orbital (1–3). Hence, d electronic configurations of central atom determine principally extra stabilization of complexes.

Chromatography is one of the most important analytical techniques used to separate components of mixtures. In chromatographic separation, thin-layer chromatography (TLC) is a rapid, easy, and simple separation method extensively used for organic species but rarely used for inorganic cations. However, TLC has advantages compared with alternative methods. For instance,

components of mixture samples can be easily separated without interference. In addition, several samples can be separated simultaneously using TLC, and the positions of spots that appear can be determined with a number of different methods (5–11). There are numerous applications of TLC concerned with the qualitative and quantitative analysis of components of natural and artificial mixtures referred to in the literature (12–16).

The qualitative and quantitative analysis of Cu^{2+} , Co^{2+} , and Ni^{2+} cations in environmental media and various samples is challenging for analytical chemists because of the similarities in their properties. Therefore, they have to separate by a convenient analytical method on order to avoid from interferences anyway. There are relatively fewer applications of TLC in the literature about qualitative analysis of metallic cation mixtures (7–11).

Dithiocarbamate ligands, such as diethyldithiocarbamate (DEDTC) and pyrrolidinedithiocarbamate (PyDTC), contain N and S donor atoms. They form electrically neutral and coordinatively saturated complexes with transition metals. The structures of the Cu, Ni, or Co (M) complexes of DEDTC [$\text{M}(\text{DEDTC})_2$] and PyDTC [$\text{M}(\text{PyDTC})_2$] are given in Figure 1. These complexes cannot interact chemically with the stationary and mobile phases in TLC systems. Therefore, these ligands are used in the separation and the qualitative analysis of metallic cation mixtures by TLC (7–11). Cu (II), Ni (II), Co (II), and other transition metal complexes with dithiocarbamates have been investigated with respect to their structures, reactions, and applications in various fields, including chromatography, by using a variety of analytical techniques (17–23). Additionally, the separability and identification of some metal-DEDTC complexes have been investigated by sequential TLC-IR systems (24).

In the practice, the chromatography techniques are principally used for the qualitative analysis, quantitative analysis, purification, and separation of the components in the mixture on the applications. In the literature, the TLC properties of $\text{M}(\text{DEDTC})_2$ and $\text{M}(\text{PyDTC})_2$ ($\text{M} = \text{Cu or Co}$) complexes were also discussed in the context of the variation of stationary phase activation, mobile phase polarity, separation mechanisms, and the

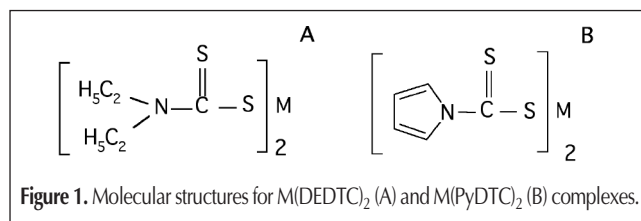


Figure 1. Molecular structures for $\text{M}(\text{DEDTC})_2$ (A) and $\text{M}(\text{PyDTC})_2$ (B) complexes.

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nature of the metal, ligand, and complexes (11). However, the chromatographic behaviors and parameters of these complexes are not discussed in the context of the linkage of CFT and TLC. According to CFT, it is expected that the stabilities of complexes are related to the interactions of complex molecules with stationary and mobile phases. In order to test cited expectation, in this study, already known separability of $M(\text{DEDTC})_2$ ($M = \text{Cu}$, Co or Ni) and $M(\text{PyDTC})_2$ ($M = \text{Cu}$ or Co) complexes with four coordination numbers by TLC (10) were reexamined for the relation of the CFT and TLC as a new approach and adaptation, and are discussed in this context of the variation of crystal field stabilization energy (CFSE), crystal field splitting energy, crystal field effect of ligands.

Experimental

Chemicals, reagents, and materials

Silica gel 60GF₂₅₄ (Si-60GF₂₅₄), NaDEDTC, NH₄PyDTC, toluene, cyclohexane, Ni(NO₃)₂, Cu(NO₃)₂, and Co(NO₃)₂ were purchased from Merck (Darmstadt, Germany).

$\text{Cu}(\text{DEDTC})_2$, $\text{Co}(\text{DEDTC})_2$, $\text{Ni}(\text{DEDTC})_2$, $\text{Cu}(\text{PyDTC})_2$, and $\text{Co}(\text{PyDTC})_2$ complexes were prepared by the reactions of NaDEDTC and NH₄PyDTC with Cu(NO₃)₂, Ni(NO₃)₂, and Co(NO₃)₂. A toluene–cyclohexane mixture (3:1, v/v) and pure toluene were used as the mobile phases. The layers of Si-60GF₂₅₄ were used as the stationary phases. The plates were prepared using Loughborough-Griffin & George TLC unikit (Leicestershire, UK). All the chemicals were of analytical grade.

Synthesis of $M(\text{DEDTC})_2$ and $M(\text{PyDTC})_2$ complexes

Prepared were 0.1 mol/L solutions of metal nitrates [Cu(NO₃)₂ and Co(NO₃)₂] at pH 5.5–6.0 (adjusted by acetic acid-sodium acetate buffer). From these solutions, a 1.0-mL aliquot was poured into a beaker and 1.0 mL of 0.1 mol/L NaDEDTC (or NH₄PyDTC) solution was added to it and then was shaken. Four milliliters of pure chloroform was added to the beaker and was shaken for 1 min. This mixture was transferred into a separatory funnel and shaken. The phases were allowed to separate for 5 min. The aqueous phase was separated from the chloroform phase and discarded. Subsequently, the chloroform phase containing the complex was dried by treating with anhydrous Na₂SO₄. The dried phase was used as sample for TLC applications.

Preparation of thin layer plates

Slurries of Si-60GF₂₅₄ in water (1:2, w/v) were spread with the spreader kit on clean glass plates measuring 7.5 × 15 cm, with a thickness of 250 μm. Non-activated plates were obtained by keeping them in a closed oven at 25°C for 12 h. They were then activated by heating in an oven at 110°C for 2 h. For TLC applications, activated plates were used.

TLC applications

Two microliter aliquots from each of the complex solutions and their mixtures were spotted with micropipettes on the starting line, which was 2.0 cm from the bottom of the activated plates. The original spots on the layers were dried at room temperature for 3 min. A pencil line was marked 5.5 cm above the

starting line of each plate. Two developing chambers with 10 × 50 × 20 cm dimensions were used for running. Sixty milliliters of the toluene–cyclohexane mixture (3:1, v/v) was poured into one chamber and 60 mL of pure toluene into the other. The lids of the chambers were closed, and the chambers were allowed to stand for 15 min to ensure that saturation of the air in each chamber with solvent vapor occurred. The plates containing the spotted samples were then carefully immersed in the developing chambers. When the solvent fronts reached 5.5 cm above the starting line of each plate, the plates were removed and dried. The migration distances of the solvent (Z_f) and of each spot (Z_x), as well as their width (W) were measured. R_f [from $R_f = Z_x/Z_f$], and N [from $N = 16(Z_x/W_x)^2$] were calculated (10,11).

Results and Discussion

The challenger Cu²⁺, Co²⁺, and Ni²⁺ in the qualitative and quantitative analysis require to be separated satisfactorily. In this context, the unidentate or polydentate ligands which contain hard N, S, or O, S donor atoms are used extensively in the separation of transition metal cations because these ligands form the coordinatively saturated stable complexes with cations, at high formation rates. In the literature, the mixture of these cations was analyzed qualitatively and separated successfully using TLC following the solvent extraction and the complexation of the cations with DEDTC ligand (10). This study (10) is evidence of the linkage between TLC and CFT. Therefore, in this study, the already known separability of Cu²⁺, Co²⁺, and Ni²⁺ cations and their complexes by TLC has been reexamined with a new approach via forming kinetically fast and thermodynamically stable complexes with respect to CFT adaptability.

DEDTC and PyDTC ligands with N, S donor atoms have been formed, the electrically neutral and coordinatively saturated stable complexes with cations cited. They cannot interact chemically with the stationary and the mobile phases in TLC systems because of their thermodynamic properties. The formation rates of complexes are very high, which also means saving time. These complexes are colored and can be easily visualized in the chromatograms (10). Furthermore, most metal complexes are expected to exhibit more or less crystal field stabilization energy (CFSE) via crystal field splitting depending on the effects of electronic configuration of central atom, structure of ligand, coordination number, and geometry of molecule.

In this work, to prepare $M(\text{DEDTC})_2$ and $M(\text{PyDTC})_2$ complexes, aqueous solutions of Cu²⁺, Co²⁺, and Ni²⁺ at pH = 5.5–6.0 (adjusted by acetic acid-sodium acetate buffer), were treated with DEDTC and PyDTC solutions. The reason for working at pH < 7 was to keep the cations in solution as the stable complexes. The complexes were extracted to the chloroform phase at pH < 7 to ensure preconcentration and cation selectivity via complexation. Moreover, as the result of organic phase extraction, the chromatographic tailing and, hence, scattering of R_f values were prevented. Chloroform was used as the organic phase because of its complex solubility and solvent volatility advantages (10).

For TLC applications, pure toluene and a toluene–cyclohexane mixture (3:1, v/v) were used as the mobile phases because of their low polarities. In addition, these solvents were chemically inert

for the complexes and surface of the thin layer. Silica gel was used most frequently as the adsorbent for the separation of coordinatively saturated complexes. Thus, Si-60GF₂₅₄ is chosen as the stationary phase (10).

The samples used were solutions of M(DEDTC)₂ and M(PyDTC)₂ complexes in chloroform. As an exception, peculiar to this study, Ni(PyDTC)₂ was not used for TLC applications. Ni(PyDTC)₂ does not reach the required concentration in the chloroform phase by virtue of its low solubility, hence it was impossible to observe its spot on the chromatograms with the naked eye. The solubilities of M(PyDTC)₂ and M(DEDTC)₂ in chloroform were higher when compared with the solubility of Ni(PyDTC)₂ in chloroform. As seen from Figure 2, M(DEDTC)₂ and M(PyDTC)₂ could be easily identified because of their distinctive colors (10).

Chromatograms of M(DEDTC)₂ and M(PyDTC)₂ complexes on activated Si-60GF₂₅₄ layers with pure toluene and a toluene–cyclohexane mixture (3:1, v/v) are shown in Figure 2. As appear in these figures, the spots of complexes and their mixtures were developed without any tailing or decomposition and were separated into their components. This chromatographic property is peculiar to electrically neutral and coordinatively saturated dithiocarbamate complexes because they are thermodynamically stable. *R_f* and *N* values for these complexes are given in Table I (10).

As seen from Table I, the *R_f* and *N* values of M(DEDTC)₂ and M(PyDTC)₂ complexes were sufficiently different from each other for TLC applications using two different mobile phases, and were separated chromatographically. In addition, the positions of their spots were determined from the chromatograms in Figure 2 by the naked eye. As a result, a mixture containing M(PyDTC)₂ or M(DEDTC)₂ could be analyzed qualitatively using TLC. Thus, a mixture containing Cu²⁺ and Co²⁺ could be ana-

lyzed qualitatively using TLC following the complexation of the cations in sample with NH₄PyDTC or NaDEDTC, and a mixture containing Cu²⁺, Ni²⁺, and Co²⁺ could be analyzed qualitatively using same procedure with NaDEDTC. On the other hand, although TLC application using pure toluene as the mobile phase is more successful than toluene–cyclohexane mixture (3:1, v/v) because of the higher *N* values belonging to complexes, either of the mobile phases can be used successfully for qualitative analysis and separation of M(DEDTC)₂ complexes as to the relative *N* values. The same judgment is valid for cations as well (10).

As a final evaluation of data in Table I regarding qualitative analysis and separation of Cu(II), Ni(II), and Co(II) complexes, it can be said that the best TLC application is performed on an activated Si-60GF₂₅₄ layer with pure toluene as the mobile phase. Additionally, the DEDTC ligand is more successful than the PyDTC ligand (10).

On the other hand, as well as dealing with chromatographic separability of the cations and their complexes, the variation of crystal field stabilization energies, crystal field splitting energies in this context of the effect of electronic configurations of central metal atoms and crystal field effect of ligands must be taken into account as an explanatory tool for the total behavior pattern of the chromatographic system, which is the focal point of this study.

As seen in Table I, the *R_f* values of Cu(DEDTC)₂ and Co(DEDTC)₂ complexes were different, although the stationary phase, mobile phase coordination number, geometry, and ligands of complexes were the same. This results from the variation of crystal field stabilization energies, and crystal field splitting energies in this context of the difference in electronic structures of Cu(II) and Co(II) as CFT. The result was also valid for Cu(PyDTC)₂ and Co(PyDTC)₂ complexes in all the other chromatographic systems.

According to Table I, the *R_f* values of Cu(DEDTC)₂ and Cu(PyDTC)₂ complexes were different when the DEDTC ligands were replaced by the PyDTC ligand, although stationary phase, mobile phase, coordination number, geometry, and metal atom of complexes were the same. This results from the variation of crystal field stabilization energies, and crystal field splitting energies in this context of the difference in crystal field effects of DEDTC and PyDTC ligands as CFT. The result was also valid for Co(DEDTC)₂ and Co(PyDTC)₂ complexes in all the other chromatographic systems.

As seen in Table I, the *R_f* value of the Cu(DEDTC)₂ complex decreased when pure toluene were replaced by the toluene–cyclohexane mixture (3:1, v/v) as the mobile phase,

when stationary phase, coordination number, geometry, and metal atom of complex were the same. This results from the variation of crystal field stabilization energies, crystal field splitting energies in this context of the difference in polarity of pure toluene and toluene–cyclohexane mixture (3:1, v/v) as CFT. The result was also valid for other complexes in all the other chromatographic systems.

In a chromatographic application, the retention mechanism depends on the liquid preadsorbed on the layer's surface, the nature

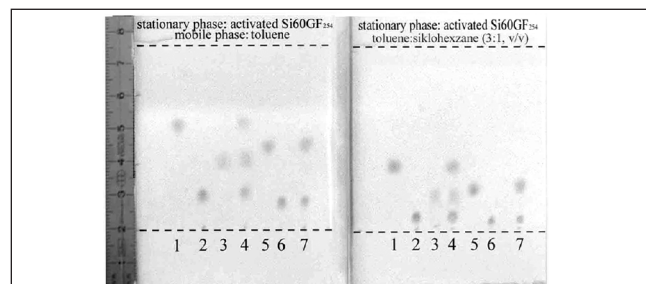


Figure 2. Chromatograms of the complexes and their mixtures: 1, Cu(DEDTC)₂; 2, Co(DEDTC)₂; 3, Ni(DEDTC)₂; 4, the mixture of 1, 2, and 3; 5, Cu(PyDTC)₂; 6, Co(PyDTC)₂; 7, mixture of 5 and 6.

Table I. *R_f* and *N* Values of M(DEDTC)₂ and M(PyDTC)₂ Spots on Activated Si-60GF₂₅₄ Layers Using Pure Toluene and Toluene–Cyclohexane Mixture (3:1, v/v)

| Complex | Running Time | I* <i>R_f</i> (X ± SD) | II* <i>R_f</i> (X ± SD) | I* <i>N</i> | II* <i>N</i> | Color |
|------------------------|--------------|-------------------------------------|--------------------------------------|----------------|-----------------|-------|
| Cu(DEDTC) ₂ | 12 | 0.55 ± 0.03 | 0.33 ± 0.02 | 1600 | 1296 | Brown |
| Co(DEDTC) ₂ | 12 | 0.18 ± 0.01 | 0.07 ± 0.01 | 178 | 64 | Green |
| Ni(DEDTC) ₂ | 12 | 0.36 ± 0.02 | 0.18 ± 0.01 | 711 | 400 | Green |
| Cu(PyDTC) ₂ | 12 | 0.44 ± 0.02 | 0.18 ± 0.01 | 1024 | 400 | Brown |
| Co(PyDTC) ₂ | 12 | 0.15 ± 0.01 | 0.04 ± 0.01 | 114 | 16 | Green |

* I = pure toluene and II = toluene–cyclohexane mixture (3:1, v/v).

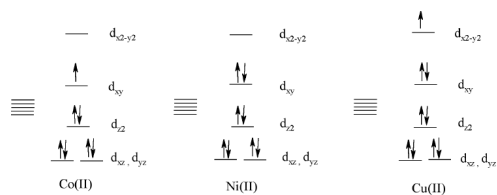
of the mobile phase and the properties of the sample components (11). In this context, the surfaces of the activated Si-60GF₂₅₄ and other layers were not covered by water or another solvent and adsorption equilibria were established between the stationary and mobile phases, as in solid-liquid chromatography (SLC). Therefore, adsorption equilibria are established, as in SLC, on the basis of the retention mechanisms of M(DEDTC)₂ and M(PyDTC)₂ complexes on all layers of Si-60GF₂₅₄.

According to Table I, although the ligands, the mobile and stationary phases are the same, the great and significant difference in the R_f values of either group complexes results from the difference in the electronic structures of the metal atoms. For example, for pure toluene as the mobile phase, R_f values of Cu(DEDTC)₂, Cu(PyDTC)₂, and Co(DEDTC)₂ 0.55 ± 0.03 , 0.44 ± 0.02 , and 0.18 ± 0.01 , respectively. The R_f difference of Cu (II) complexes is 0.11, whereas the R_f difference of Cu(DEDTC)₂ and Co(DEDTC)₂ is 0.37. The difference stemmed from that the metal of complexes is higher than those from ligand. This result demonstrates that the contribution of ligands to TLC behaviors of these complexes is slight and the numerical difference stemmed from metal of complexes is higher, more drastic, and more dramatic than those from ligand. It is necessary to get a very fundamental and powerful explanation for this influential change.

The dithiocarbamate compounds and their complexes play an important role in inorganic chemistry and technology areas such as rubber, flotation, agriculture, medicine, lubrication, etc. Therefore, the studies on dithiocarbamate chemistry have attracted much interest for about one hundred years. Depending on experimental preparation conditions, some dithiocarbamate complexes of transition metals can adopt both mono- and binuclear types of molecular structures (25,26). Both monomeric and dimeric complex species were investigated by a variety of experimental techniques so far. M(DEDTC)₂ and M(PyDTC)₂ complexes have mononuclear square-planar molecular structures while the dimeric species have non-planar configurations of the coordination polyhedra of the central atom (distorted tetrahedral, trigonally-bipyramidal, or square-pyramidal) (26–31).

While the charges, radii, and charge densities of Co²⁺, Ni²⁺, and Cu²⁺ in aqueous solutions are close each other, their d⁷, d⁸, and d⁹ electronic configurations belong to these cations lead to the different physical and chemical properties of the complexes. In this context, CFT says that the ligand field splittings of complexes with the symmetry square planar geometry and the orbital schemes are as on Figure 3. As seen in Figure 3, the e_g and t_{2g} orbitals in the octahedral field are split again by changing of the number and orientation of ligands approaching in square planar fashion. The relative energies of orbitals in the terms CFSE (Δ_0) are 12.28, 2.28, -4.28, -5.14, and -5.14 Dq for d_{x²-y²}, d_{xy}, d_{z²}, and

d_{xy}, respectively (3). Thus, it is expected that 7, 8, and 9 electrons of Co²⁺, Ni²⁺, and Cu²⁺ cations, respectively, Co(DEDTC)₂, Ni(DEDTC)₂, Cu(DEDTC)₂, Co(PyDTC)₂, and Cu(PyDTC)₂ complexes with square planar geometry are populated to splitting d orbitals as follows:



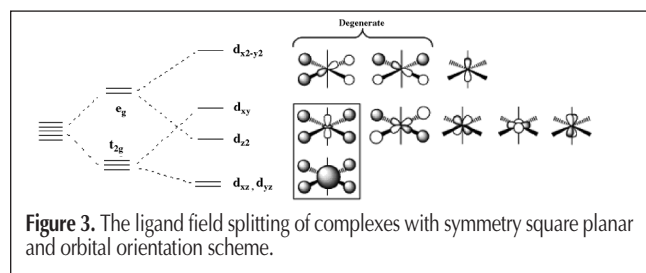
It followed that because of these d electron distributions in metal complexes with same ligand, coordination number, and geometry, the extra stabilization energies decrease in the order of Co²⁺, Ni²⁺, and Cu²⁺. Hence, the interactions of the corresponding complex molecules with the stationary phase decrease, though the interactions with the mobile phase increase in the same order. According to Table I, while coordination number, geometry, and kind of ligand for Co(DEDTC)₂, Ni(DEDTC)₂, and Cu(DEDTC)₂ complexes are the same, their R_f values for the TLC application using pure toluene as the mobile phase are 0.18 ± 0.01 , 0.36 ± 0.02 , and 0.55 ± 0.03 , respectively. These R_f values reveal that the interactions with stationary phase of these complexes have been decreasing in the order of Co²⁺ (d⁷), Ni²⁺ (d⁸), and Cu²⁺ (d⁹). Similarly, the R_f values of Co(PyDTC)₂ and Cu(PyDTC)₂ complexes are 0.15 ± 0.01 and 0.44 ± 0.02 , respectively. This relationship was also valid for these metals and their complexes in all the other chromatographic systems. As a result, when the extra stabilization energies of these complexes decrease, the interactions with stationary phase of these complexes decrease although the interactions with mobile phase of these complexes increase. Consequently, it is possible to say that the separation of these complexes by the TLC is the coordination chemistry.

Conclusion

This study was carried out on mixtures of M(DEDTC)₂ and M(PyDTC)₂ complexes in order to understand the linkage between the TLC and the CFT and to reexamine the known separability of Co²⁺, Ni²⁺, and Cu²⁺ cations using TLC following the complexation of the cations with DEDTC and PyDTC ligands. In light of this study, conclusions are as follows:

(i) CFT is very appropriate tool to explain the very different R_f values of complexes and their chromatographic behavior. The interaction of metal complexes with the stationary and mobile phases in TLC is determined by electronic configurations of the metal atoms and the ligand field effect of square planar geometry in complexes. While the charge, radii, and charge density of Co²⁺, Ni²⁺, and Cu²⁺ cations in aqueous solutions are close to each other, the crystal field stabilizations stemmed from their d⁷, d⁸, and d⁹ electronic configurations respectively lead to different physical, chemical, and chromatographic properties of the complexes.

(ii) While the mobile phase, the stationary phase, and coordination number, and geometry of complexes except kind of ligand are the same, the R_f values of two group complexes are signifi-



cantly different greatly because of crystal field effect of ligands and the extra stabilization energies.

(iii) While coordination number, the geometry, and the kind of ligand in the complexes are the same, the extra stabilization energies of the metal complexes decrease in order Co^{2+} (d^7), Ni^{2+} (d^8), and Cu^{2+} (d^9) because of these d electron distributions. Hence, the interactions of complexes decrease with the stationary phase, though the interactions with the mobile phase increase in the same order. This relationship is valid for these metals and their complexes in all of the chromatographic systems.

(iv) The R_f value of $\text{M}(\text{DEDTC})_2$ and $\text{M}(\text{PyDTC})_2$ complexes decrease when pure toluene was replaced by the toluene–cyclohexane mixture (3:1, v/v) as the mobile phase, and when the stationary phase, coordination number, geometry, metal atom of complex were the same. This results from the variation of crystal field stabilization energies, crystal field splitting energies in this context of the difference in polarity of pure toluene and toluene–cyclohexane mixture (3:1, v/v) as CFT.

(v) The R_f values for $\text{M}(\text{DEDTC})_2$ and $\text{M}(\text{PyDTC})_2$ complexes with four coordination numbers of Cu(II), Ni(II) and Co(II) reveal the relationship between the TLC and the CFT on the coordination chemistry. Consequently, it is possible to say that the separation of these complexes by the TLC is the coordination chemistry.

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