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THIN-LAYER AND FILTER PAPER CHROMATOGRAPHY OF METAL COMPLEXES AND SOME NON-METAL COMPOUNDS

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CONTENTS

LIGAND ABBREVIATIONS

AA^iUH = 1-amidino-*O*-isoamylurea
AA^nUH = 1-amidino-*O*-n-amylurea
AB^iUH = 1-amidino-*O*-isobutylurea
AB^nUH = 1-amidino-*O*-n-butylurea
acacH = acetyl acetone
AcH = acetic acid

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AEUH = 1-amidino-*O*-ethylurea
α-alanH = α-alanine
β-alanH = β-alanine
AMUH = 1-amidino-*O*-methylurea
AP^iUH = 1-amidino-*O*-isopropylurea
AP^nUH = 1-amidino-*O*-n-propylurea
BigH = biguanide
CO_3H_2 = carbonic acid
DESO = diethyl sulfoxide
dien = diethylenetriamine
dipy = α,α'-dipyridyl
DMS = dimethyl sulfide
DMSO = dimethyl sulfoxide
$EDDAH_2$ = ethylenediamine *N,N'*-diacetic acid
EDHPA = ethylenediamine *N,N'*-bis(2-hydroxyphenylacetic acid)
en = ethylenediamine
Et-BigH = ethyl biguanide
Et_2-BigH = diethyl biguanide
$Et(BigH)_2$ = ethylene dibiguanide
Et_4-dien = *N,N,N',N'*-tetraethyldiethylenetetramine
glyH = glycine
histH = histidine
$IDAH_2$ = iminodiacetic acid
leucH = leucine
$lutH_2$ = lutidinic acid
Me-BigH = *N*-methyl biguanide
Me_2BigH = *N',N'*-dimethyl biguanide
methH = methionine
o-phen = *o*-phenanthroline
OXH_2 = oxalic acid
Ph-BigH = *N'*-phenyl biguanide
PicH = picolinic acid
Pn = propylenediamine
Pr^i-BigH = *N'*-isopropyl biguanide
Py = pyridine
ValH = Valine

A. INTRODUCTION

It has been only in recent years that chromatographic techniques have found widespread use in investigating different areas of the chemistry of metal complexes. Indeed, both thin-layer chromatography (TLC) and filter paper chromatography have been extensively applied by coordination chemists.

More than a decade ago Druding and Kauffman [1] made a general survey of the chromatography of coordination complexes. In the present article we consider some aspects of the chromatography of metal complexes that were not discussed in Druding and Kauffman's review. We have tried to include all the important studies that have appeared during the last ten years (1968—1977), with particular emphasis on TLC and filter paper chromatography.

Most TLC and paper chromatographic studies have involved cobalt(III) complexes, whereas little work on complexes of other metals has been reported. Cobalt(III) complexes, being substitution inert, lead to a minimum of complicated substitution reactions with developer solvents. Chromium(III) complexes have been little investigated on paper and TLC, presumably because they cannot be synthesized as easily as those of cobalt(III) and also because a good spot test reagent is not yet available for chromium(III). Furthermore, chromatographic studies of complexes of dipositive metal ions such as copper(II), nickel(II), palladium(II) and platinum(II) are still quite scarce [2—10]. Chromatographic studies of copper(II) and nickel(II) complexes might be complicated but interesting because of their substitution—labile character and their ability to adopt several configurations. Some studies dealing with the chromatography of genuine square planar complexes of these two metal ions [4,6] have recently appeared in the literature.

Chromatographic behavior of any series of charged complexes is likely to be determined by a number of factors such as (1) charge, (2) solubility, (3) composition of the mobile and stationary phases and (4) outer-sphere association. Almost all the reports dealing with these factors may be credited to Yoneda [11—16] and to Dutta and Ray [4—7,17,18].

In view of the tendency of a mixed chelate to disproportionate into the respective homochelates, particularly in solution, synthesis of such mixed chelates is often quite difficult. Nevertheless, in addition to providing interesting information on the magnetism, electronic spectra and flexidentate behavior of the coordinating ligands, syntheses of mixed chelates have also revealed interesting chromatographic behavior.

Since the publication of Druding and Kauffman's 1968 review [1], Kauffman and co-workers have also achieved separations of inorganic isomers of a very wide range, covering many unusual non-metal compounds and complexes with unusual ligands. These are dealt with at appropriate places in this review.

B. THIN-LAYER CHROMATOGRAPHY

Most TLC studies of complexes have so far been carried out with silica gel as the stationary phase, while cellulose, alumina, starch and other adsorbents have been used only sparsely [1].

It is now an established fact that the silanol group (≡Si—OH) of hydrated silica gel is weakly acidic and has cation exchange properties [19—22]. The sorption of cationic metal complexes on silica gel has been studied extensively by Vydra and Marková [23—26], who observed that over a wide range of pH, the amount of liberated acid corresponds to the charge of the complex ion

$$m(\equiv\text{Si-OH}) + \text{M}^{n+} \rightleftharpoons \text{M(O-Si}\equiv)_m^{(n-m)+} + m\text{H}^+$$

The fact that the adsorbed metal ions cannot be removed by mere washing with water bears testimony to the coordination of the silanol oxygen via exchange of the hydrogen atoms by the metal ion [19,27,28].

In the following sections we describe some recent applications of TLC to coordination chemistry.

(i) Separation of metal complexes

(a) Complexes of the same metal ion with different charges

Successful separation of a large number of di- and tripositive cobalt(III) complexes (e.g., $[\text{Co(en)}_2(\text{H}_2\text{O})\text{F}]^{2+}$ and $[\text{Co(en)}_2(\text{H}_2\text{O})_2]^{3+}$) on silica gel was achieved with a HCHO—CH_3OH developer solvent containing acetic acid to repress hydrolysis [29]. Use of this solvent permitted differentiation between $[\text{Co(NH}_3)_5\text{Cl}]^{2+}$ and the *cis* and *trans* isomers of $[\text{Co(NH}_3)_4(\text{H}_2\text{O})\text{Cl}]^{2+}$, although all of these species possess the same charge (Table 1).

In agreement with Yoneda's earlier results [11], Dutta and Ray [17,18,30] noted that, on using distilled water as the mobile phase, neutral and anionic cobalt(III) complexes travel easily on the silica gel bed close to the solvent front, whereas cationic complexes diffuse from the point of application. Silica gel is charged negatively in water so that the anionic stationary phase adsorbs the cationic complexes more than the neutral ones, while the anionic complexes are allowed to travel almost unhindered to the solvent front.

(b) Complexes of the same metal ion with the same charge but with variation in the coordination sphere

Jursík [34] separated some neutral nickel(II) amino acid chelates from one another on silica gel using aqueous phenol as developer. Interestingly, R_F values increased with increase in the number of carbon atoms present in the chelate molecule (R_F values of $[\text{Ni(gly)}_2] = 0.17$, $[\text{Ni}(\alpha\text{-alan})_2] = 0.24$, $[\text{Ni(val)}_2] = 0.38$, etc.). Moreover, chelates formed with amino acids having n-alkyl chains showed higher R_F values than those containing branched side chains. Furthermore, the chelates formed with tridentate ligands (except histidine) exhibited low R_F values, which indicated that the energy of formation of the hydrogen bond between the silanol- or silandiol-active silica gel sites and the solute exceeded the energy of solvation.

In this connection, it may be mentioned here that Dutta and Ray [17,18] observed in paper chromatographic studies that $[\text{Ni(BigH)}_2]\text{Cl}_2$ always registered higher R_F values than the corresponding $[\text{Ni(Et—BigH)}_2]\text{Cl}_2$ (R_F values: $[\text{Ni(BigH)}_2]\text{Cl}_2 = 0.78$ and $[\text{Ni(Et—BigH)}_2]\text{Cl}_2 = 0.52$ in aqueous KCl—pyridine developer).

Yoneda's [15] experiments on $[\text{Co(NH}_3)_6]\text{Cl}_3$, $[\text{Co(NH}_3)_4(\text{en})]\text{Cl}_3$, [Co-

TABLE 1

TLC separation of different complexes of the same metal but of varying overall charge

Complex	Stationary phase	Purpose	Ref.
Cobalt(III) ammines	TLC (silica gel) TLC (alumina)	separation; charge identification	1, 12—14 29, 31, 32
Cobalt(III) EDDA	TLC (silica gel)	separation	33
$[Co(BigH)_3]Cl_3$	TLC (silica gel)	separation; charge identification	17, 18
$[Co(Ph\text{-}BigH)_3]Cl_3$	TLC (silica gel)	separation; charge identification	17, 18
$[Co(X)(BigH)_2]Cl_3$ (X = o-phen, dipy)	TLC (silica gel)	separation; charge identification	17, 18
$[Co(X)(BigH)_2]Cl_2$ (HX = glyH, α-alanH; leucH, methH, histH, picH)	TLC (silica gel)	separation; charge identification	17, 18
$[Co(X)(BigH)_2]Cl$ (X = IDA^{2-}; CO_3^{2-})	TLC (silica gel)	separation; charge identification	17, 18
$[Co(NH_3)_3(NO_2)_3]$	TLC (silica gel)	separation; charge identification	17, 18
$K[Co(gly)_2(NO_2)_2]$	TLC (silica gel)	separation; charge identification	17, 18
$NH_4[Co(NH_3)_2(NO_2)_4]$	TLC (silica gel)	separation; charge identification	17, 18
$Na_3[Co(NO_2)_6]$	TLC (silica gel)	separation; charge identification	17, 18
$K_3[Co(OX)_3]$	TLC (silica gel)	separation; charge identification	17, 18
$[Co(en)_2(H_2O)(Ac)]^{2+}$	TLC (silica gel)	separation	29
$[Co(en)_2(Ac)_2]^+$	TLC (silica gel)	separation	29
$[Co(NH_3)_5(N_3)]^{2+}$	TLC (silica gel)	separation	29
$[Co(NH_3)_6]^{3+}$	TLC (silica gel)	separation	29
$[Co(en)_2XL]^{2+}$	TLC (silica gel)	separation	36
$[Co(L)_4XY]^+$ (L = amine; X and Y = Cl, Br, I, SCN, etc.)	TLC (silica gel)	separation	36
$[Co(diOXH)_2XY]^-$ ($diOXH_2$ = dimethylglyoxime, benzyldioxime, etc.)	TLC (silica gel)	separation	34
$[NiL_2]$ (HL = glyH, α-alanH, ValH, leucH, methH, iso-leucH, etc.)	TLC (silica gel)	separation	34
$[Cr(L)_4XY]^+$	TLC (silica gel)	separation	36
$[Cr(NCS)_4(L)_2]^-$ (L = amine; X,Y = Cl, Br, I, etc.)	TLC (silica gel)	separation	36
$[Cu(BigH)_2]Cl_2$	TLC (silica gel)	separation	17, 18
$[Cu(X\text{-}BigH)_2]Cl_2$ (X = CH_3-, C_2H_5-, C_3H_7-, C_6H_5-, etc.)	TLC (silica gel)	separation	17, 18
$[Cu(X)(BigH)]Cl_2$ (X = o-phen, dipy)	TLC (silica gel)	separation; charge identification	17, 18
$[Cu(X)(BigH)]Cl$ (HX = glyH, α-alanH)	TLC (silica gel)	separation; charge identification	17, 18
$[Cu(gly)(dipy)]Cl$	TLC (silica gel)	separation; charge identification	17, 18
$[Cu(gly)(o\text{-}phen)]Cl$	TLC (silica gel)	separation; charge identification	17, 18
$[Cu(X)(IDA)]$ (X = o-phen, dipy, BigH)	TLC (silica gel)	separation; charge identification	17, 18
Rhodium(III) EDDA	TLC (silica gel)	separation	33
Platinum(II) EDDA	TLC (silica gel)	separation	31
$[Pd(X\text{-}BigH)_2]Cl_2$ (X = CH_3-, C_2H_5-, C_6H_5-)	TLC (silica gel)	separation	17, 18

TABLE 2

TLC separation of *cis—trans* isomers

Complex	Stationary phase	Relative mobility	Ref.
$[Cr(OX)_2(H_2O)_2]^-$	TLC (silica gel)	*cis* ⩾ *trans*	56
$K[Cr(H_2O)_2(C_2O_4)_2]$	TLC (silica gel)	*trans* > *cis*	41
$[Cr(en)_2(NCS)_2]SCN$	TLC (silica gel)	*trans* > *cis*	41
$[Cr\{(+)(-)\text{-}Pn\}_2(NCS)_2]SCN$	TLC (silica gel)	*cis* > *trans*	41
$[Cr(Py)_3Cl_3]$	TLC (silica gel)	*trans* > *cis*	41
$[Cr(CO)_3(CH_3OC_6H_4COOCH_3)]$ (a) *p*-methoxy (b) *o*-methoxy	TLC (silica gel)	*o*-methoxy > *p*-methoxy	46
$[Cr(CO)_3(ClC_6H_4COOCH_3)]$ (a) *p*-chloro (b) *m*-chloro	TLC (silica gel)	*m*-Cl > *p*-Cl	46
$[Co(en)_2X_2]^+$ ($X = Cl^-, NO_2^-$)	TLC (cellulose)	*cis* > *trans*	39
$[Co(NH_3)_4(NO_2)_2]^+$	TLC (cellulose)	*cis* > *trans*	39
$[Co(en)_2Cl_2]^+$	TLC (ZnS)	*trans* > *cis*	35
[Co(S-(+)-α-alan)$_3$]	TLC (silica gel)	*mer*(N) > *face*(N)	38
$[Co(gly)_3]$	TLC (cellulose)	*trans* > *cis*	37
$[Co(acac)_2(NO_2)Py]$	TLC (silica gel)	*cis* > *trans*	41
[Co(acac)$_2$(NO$_2$)(4-*tert*-butylpyridine)]	TLC (silica gel)	*cis* > *trans*	41
$[Co(en)_2(X\text{-}NH_2)Cl]Cl_2$ ($X = CH_3—, C_2H_5—, C_3H_7—$)	TLC (silica gel)	*trans* > *cis*	41
$[Co(en)(gly)_2]$	TLC (silica gel)	*cis* > *trans*	41
$L\text{-}[Co\{(-)\text{-}Pn\}_3]Br_3$	TLC (silica gel)	*trans* >> *cis*	41
$[Cu(lutidine)_4]Cl_4$ (a) 3,4-lutidine (b) 3,5-lutidine	TLC (silica gel)	(b) > (a)	46
$[Cu(tyrosinate)_2]$	TLC (silica gel)	*trans* > *cis*	42
[Fe{*N*-1-(2′-pyridyl)ethylidene-aniline}$_3$](ClO$_4$)$_2$	TLC (silica gel)	*trans* > *cis*	41
[Fe{*N*-1-(2′-pyridyl)ethylene-*p*-phenylenediamine}$_3$](ClO$_4$)$_2$	TLC (silica gel)	*trans* > *cis*	41
[Fe{*N*-1-(2′-pyridyl)benzylidene-aniline}$_3$](ClO$_4$)$_2$	TLC (silica gel)	*trans* > *cis*	41
[Fe(*N*-tolylsalicylideneimine)$_2$]$_2$O (a) *m*-tolyl (b) *p*-tolyl	TLC (silica gel)	(b) > (a)	46
[Fe(*N*-chlorophenylsalicylidene-imine)$_2$]O (a) *m*-chloro (b) *p*-chloro	TLC (silica gel)	(b) > (a)	46
$[Fe(NCC_6H_4\text{-}p\text{-}CH_3)_4Cl_2]$	TLC (silica gel)	*trans* > *cis*	41
$[Rh(Py)_3Cl_3]$	TLC (silica gel)	*trans* >> *cis*	41
$[Rh(O\text{-}As)_3Cl_3]$ (O-As = methoxyphenyl-dimethylarsine (a) *p*-(O-As) (b) *m*-(O-As)	TLC (silica gel)	(b) > (a)	46

TABLE 2 (*continued*)

Complex	Stationary phase	Relative mobility	Ref.
$[Ir(Ph_3P)_3HCl_2]$	TLC (silica gel)	*trans* > *cis*	41
$[Ir(H_2O)(Py)_2Cl_3]$	TLC (silica gel)	*trans* >> *cis*	41
$[Ir(Ph_3P)_2(CO)Cl]$	TLC (silica gel)	*trans* >> *cis*	42
$[SnI_4 \cdot OS(C_2H_4)_2SO]$	TLC (silica gel)	*cis* > *trans*	46
$[Sn(Ph)_2Cl_2X]$ (X = *cis*, 1,4-dithian 1,4-dioxide, $OS(C_2H_4)_2SO$)	TLC (silica gel)	*trans* >> *cis*	41
$[W(PP)(CO)_4]$ (PP = 2-*cis*- or *trans*-propenyldiphenylphosphine)	TLC (silica gel)	*trans* > *cis*	46
$[Pt(Et_2S)_2Cl_4]$	TLC (silica gel)	*trans* > *cis*	41
$[Pt(n\text{-}Bu_3P)_2Cl_4]$	TLC (silica gel)	*trans* > *cis*	41
$[Pt(gly)_2]$	TLC (silica gel)	*trans* > *cis*	42
$[Pt(thiosemicarbazide)_2]^{2+}$	TLC (silica gel)	*cis* > *trans*	42
$[Pd(thiosemicarbazide)_2]^{2+}$	TLC (silica gel)	*trans* > *cis*	42
$[Pt(n\text{-}Bu_2S)_2Cl_2]$	TLC (silica gel)	*trans* > *cis*	57
$[Pt(iso\text{-}Bu_2S)_2Cl_2]$	TLC (silica gel)	*trans* > *cis*	57
$[Pt(tert\text{-}Bu_2S)_2Cl_2]$	TLC (silica gel)	*trans* > *cis*	57
trans-$[Pt(Bu_2S)_2Cl_2]$	TLC (silica gel)	n > tert iso > tert n > iso > sec	57
$[Pt(Bu_2S)_2Cl_2]$	TLC (silica gel)	*trans*-n and *trans*-iso > *trans*-sec > *trans*-tert > *cis*-n and *cis*-iso > *cis*-tert	57

$(en)_3]Cl_3$, $[Co(dipy)_3]Cl_3$, etc. on an alumina bed using aqueous NaCl—Na_2SO_4 solution showed a regular increase in R_F with decreasing number of N—H bonds within the complex. The degree of hydration decreases with decreasing number of N—H bonds within the complex.

Kakushkin et al. [35] separated "face" and "edge" isomers of dimethyl sulfide—rhodium(III) complexes from one another by using ZnS as the stationary phase and C_6H_6—$CHCl_3$ as the mobile phase. Interestingly, the "face" isomer was retained on ZnS, while the "edge" isomer reached the solvent front.

Generally, the greater retentivity of the *cis* isomer (lower R_F) than the corresponding *trans* isomer on the silica gel bed (or resin) is probably due to the presence of two adjacent points of attachment of the *cis* isomer to the silanol sites of the silica gel (i.e., bidentate behavior of silica gel). On the other hand, the *trans* groups, being on opposite sides of the complex, can attach at one point only [1,19] (i.e., monodentate behavior of silica gel). Moreover, if one assumes the adsorption mechanism, then this trend should also prevail because the *cis* isomer is more polarized than the *trans* isomer [1,19]. However, contrary to the above line of argument, a reverse order of R_F values is also reported in the literature (Table 2).

The differences in R_F values for *cis—trans* isomers may have their origins in the differences in (1) dipole moment, (2) solubilities, (3) ion-pair formation between the complex and the salt-containing developer, (4) stability of the complexes, (5) steric hindrance, (6) adsorptivity and (7) symmetry [1,3,8, 29,31,38—44]. Table 2 shows the salient features of some such separations.

(c) Diastereoisomers

Chromatographic methods have been shown to be quite useful for resolution of many racemic mixtures. Yoneda et al. reported the resolution of racemic $[Co(en)_3]^{3+}$ by means of both TLC (silica gel) and electrophoresis [16, 43,44]. The resolution was effected by using an aqueous solution of d-tartrate anion and aluminum chloride. The mechanism of separation was based on the different degree of ion-pair formation between d-$[Co(en)_3]^{3+}$ or l-$[Co(en)_3]^{3+}$ on the one hand and d-tartrate on the other. The $AlCl_3$ was supposed to have reduced the degree of hydration of each ion because of its large hydration energy, thus assisting in the separation.

Haworth and Hung [45] successfully separated the diastereoisomers of $[Co(en)_3]^{3+}$ using optically active quartz incorporated into TLC plates containing cellulose and sodium potassium tartrate with $AlCl_3$ as the developer. It appears likely that $AlCl_3$ plays the same dehydrating role as it did in Yoneda's resolution [16,43,44].

(d) Various inorganic isomers

Recently Kauffman and his group and others have successfully separated several inorganic isomers such as ligand isomers of various coordination numbers; structural, linkage, geometric and conformational isomers of various coordination numbers; and isomers of non-metals (Table 3) [40—42,46—56]. Successful separation and identification of a variety of isomers of a series of the non-metals boron, silicon and phosphorus stand out as a novel achievement. More recently, Kauffman et al. synthesized and characterized the eight possible isomers of dichlorobis(dibutyl sulfide)platinum(II), six of them in a pure state (*cis*- and *trans*-n, *cis*- and *trans*-iso, and *cis*- and *trans*-sec) [57]. They also separated some of the geometric isomers from each other, some of the ligand isomers from each other, and some of both types from each other by TLC (Table 2).

(ii) The role of adsorbents and developers in influencing the composition, stereochemistry and structure of coordination complexes

Burwell et al. [19] have shown that prolonged contact of some cobalt(III) complexes with silica gel (stationary phase) containing basic solvents as developers results in a change in stereochemistry and substitution of the

TABLE 3

TLC separation of isomers of the non-metals boron, phosphorus and silicon on silica gel [48]

Compound	Stationary phase	Mobile phase	Type of separation
$(R_3 \cdot NH \cdot BH_2)_3$ (a) *cis* (white) (b) *trans* (white) ($R = CH_3$—, C_2H_5—)	TLC (silica gel)	CH_2Cl_2	complete
$B_{10}H_{10}C_2H_2$ (a) *o*-carborane (b) *m*-carborane	TLC (silica gel)	CCl_4, $(C_2H_5)_2O$	complete
$B_{10}H_8Br_2 \cdot C_2H_5$ (a) 9,10-dibromo-*o*-(white) (b) 9,10-dibromo-*m*-(white)	TLC (silica gel)	$(C_2H_5)_2O$	complete
$P_4N_4(C_6H_5)_6[N(CH_3)_2]_2$ (mixture of *cis*—*trans*; pure isomers were not available so the species were not identified)	TLC (silica gel)	C_6H_6, $(CH_3)_2CO$: CCl_4(1 : 4)	complete
$P_4N_4(C_6H_5)_4(OC_6H_5)_2Cl_2$ (two isomers)	TLC (silica gel)	CH_2Cl_2, $CHCl_3$	partial
$P_4N_4(C_6H_5)_4Cl_4$ (*cis*—*trans*)	TLC (silica gel)	CCl_4	complete
$P_3N_3(C_6H_5)_2(OC_6H_5)_2Cl_2$ (two isomers)	TLC (silica gel)	$CHCl_3$, CCl_4	complete
$P_3N_3(OC_6H_5)_4Cl_2$ (*cis*—*trans*)	TLC (silica gel)	CCl_4	complete
$P_3N_3F_4(C_6H_5)_2$ (*cis*—*trans*)	TLC (silica gel)	$CHCl_3$, n-C_5H_{12}: $CHCl_3$(1 : 1)	partial
$P_3N_3Br_4[N(CH_3)_2]$ (*cis*—*trans*)	TLC (silica gel)	$(CH_3)_2CO$, CH_3OH	partial

ligand.

$$\begin{tikzcd} \textit{trans}\text{-Co(en)}_2\text{Cl}_2^{+}\text{O}^{-}\text{—Si}\equiv \arrow[r] \arrow[d, "\substack{H_2O \\ \text{(ads.)}}"'] & \textit{trans}\text{-Co(en)}_2\text{ClO—Si}^{+}\equiv\text{Cl}^{-} \\ \textit{cis}\text{-Co(en)}_2(\text{H}_2\text{O})\text{Cl}^{2+}\text{O}^{-}\text{—Si}\equiv\text{Cl}^{-} & \end{tikzcd}$$

Reaction of *cis*-$Co(en)_2(H_2O)Cl^{2+}$ to form *cis*-$Co(en)_2ClO—Si\equiv^+$ may proceed, presumably via an intermediate five-coordinate species $Co(en)_2Cl^{2+}$.

The cause of tailing of some nickel(II) complexes is believed [34] to be due to either strong adsorption on the silica gel bed or to the entry of the siloxy anion into the coordination sphere of the nickel(II).

Hagel and Druding [29] found that $[Co(NH_3)_5Cl]^{2+}$ has a higher R_F value than $[Co(NH_3)_4(H_2O)Cl]^{2+}$ despite their having the same charge. They argued that high retention of the aquo complex is a result of substitution of the aquo group by the silanol group of the stationary phase. More interestingly, [Co$(NH_3)_4CO_3]^+$ and $[Co(NH_3)_4(NO_3)_2]^+$ exhibit low R_F values (~0.3) although both of them carry a +1 charge. The authors [31] claimed that the complexes are chromatographed not as genuine complexes but that they undergo secondary reactions with the silanol group, thus bringing about a change in the overall charge of the complex species.

Baba and Yoneda [58] used TLC to try to distinguish neutral octahedral and square planar complexes. With silica gel as the stationary phase and water as the mobile phase, $[Co(gly)_3]$ moved easily to the solvent front, while $[Cu(gly)_2]$ remains at the point of application. Baba and Yoneda claimed that retention of the latter complex takes place through the direct coordination of SiO_2 to the copper(II) complex giving it a six-coordinate structure. Since cobalt(III) is already coordinately saturated, SiO_2 cannot occupy any site around it. The water molecules of $[Ni(gly)_2(H_2O)_2]$ are believed to be replaced by silica gel, and thus the complex conforms to the behavior of bis(glycinato)-copper(II). Indeed, bis(glycinato)copper(II) crystallizes as a monohydrate, and its X-ray structure shows a distorted octahedral structure through coordination of the H_2O molecule along with a carboxyl oxygen of a neighboring molecule [59].

In TLC studies on silica gel with $CH_3OH—HClO_4—DMSO$ as the mobile phase, Kirk et al. [56] showed that photolysis of $[Cr(en)_2OX]^+$ ($R_F = 0.00$) to $[Cr(en)(OX)(H_2O)_2]^+$ ($R_F = 0.85$) had occurred.

On prolonged contact with a solvent, the complex may undergo solvolysis reactions which may yield a change in its configuration [60]. Thus attempted separation of *cis* and *trans* isomers of some octahedral complexes on a silica gel—starch layer revealed trace quantities of impurities although the complexes were sufficiently purified at the start. For example, *cis*- and *trans*-$[Co(NH_3)_4(NO_2)_2]^+$ betrayed the formation of a small amount of $[Co(NH_3)_3(NO_2)_3]$, while *cis*- and *trans*-$[Co(NH_3)_3(NO_2)_3]$ revealed the presence of traces of $[Co(NH_3)_4(NO_2)_2]$. These findings indicate both hydrolysis and geometric rearrangement in contact with the solvent bed.

Hathaway and Lewis [27,61,62] compared the differences in spectra of nickel(II), cobalt(II/III) and copper(II) complexes in the solid state (adsorbing the complexes on a silica gel bed) and in aqueous solution. For nickel(II) complexes, the spectral behavior of the adsorbed ion is identical with that in aqueous solution. When the ligand (N as the donor atom): nickel(II) concentration is high, a *cis*-octahedral chromophore or a five-coordinated chromophore was suggested. A reverse process was observed after aquation. The hexaaquocobalt(II) reacts with the silica gel, first forming a blue tetrahedral species and then a pink octahedral complex. On varying the experimental conditions, various species (e.g., 4-, 5- and 6-coordinate) are formed, which were confirmed by spectra. In the case of copper(II) compounds containing multidentate *N*-ligands, the most likely species on the hydrated silica gel are CuN_2O_4 (tetragonal octahedral) or CuN_2O_3 (square pyramidal).

TABLE 4

R_F values of nickel(II) complexes with different developers (TLC on silica gel) [17,18]

Complex	0.2 M KCl	0.2 M K_2SO_4	0.2 M $Na_2S_2O_3$	0.2 M KNa tartrate
$[Ni(BigH)_2]Cl_2$	0.90	0.90	0.90	0.92
$[Ni(Me\text{-}BigH)_2]Cl_2$	0.90	0.91	0.93	0.94
$[Ni(Et\text{-}BigH)_2]Cl_2$	0.89	0.92	0.92	0.92
$[Ni(Pr^i\text{-}BigH)_2]Cl_2$	0.90	0.94	0.94	0.94
$[Ni(Me_2\text{-}BigH)_2]Cl_2$	0.90	0.92	0.90	0.90
$[Ni(Et_2\text{-}BigH)_2]Cl_2$	0.88	0.91	0.89	0.90
$[Ni(Ph\text{-}BigH)_2]Cl_2$	0.89	0.92	0.89	0.91
$[Ni\{Et(BigH)_2\}]Cl_2$	0.52	[a]	0.74	[a]
$[Ni(AMUH)_2]Cl_2$	0.89	0.90	0.91	0.92
$[Ni(AEUH)_2]Cl_2$	0.89	0.90	0.93	0.94
$[Ni(AP^nUH)_2]Cl_2$	0.89	0.89	0.94	0.94
$[Ni(AP^iUH)_2]Cl_2$	0.90	0.90	0.92	0.92
$[Ni(AB^nUH)_2]Cl_2$	0.89	0.89	0.91	0.93
$[Ni(AB^iUH)_2]Cl_2$	0.90	0.90	0.93	0.94
$[Ni(AA^nUH)_2]Cl_2$	0.90	0.90	0.90	0.92
$[Ni(AA^iUH)_2]Cl_2$	0.89	0.89	0.90	0.93
$[Ni(en)_3]Cl_2$	0.84 (0.23)[b]	0.89 (0.23)[b]	0.90 (0.53)[b]	0.90
$[Ni(H_2O)_6]Cl_2$	0.90	0.92	0.93	0.93

R_F values of $[Ni(gly)_2(H_2O)_2]$ are 0.84 in 0.1 M KCl; 0.80(0.82) in 0.1 M KI; 0.90(0.85) in 1 M K_2SO_4. [a] The spot remained at the point of application. [b] Values in parentheses were reported by Yoneda [58].

(a) Nickel(II) complexes

It is interesting to note that almost all the nickel(II) complexes reported in Table 4 give R_F values (on silica gel stationary phase with developers like KCl, K_2SO_4, $Na_2S_2O_3$, etc.) that are the same as that shown by the hexaaquonickel(II) ion. *This indicates that the acid liberated from the silica gel is sufficient to destroy most nickel complexes.*

(b) Copper(II) complexes

The behavior of copper(II) complexes on silica gel is quite different from that of nickel(II) complexes. These complexes revealed R_F values which differed from complex to complex and also from that of hexaaquocopper(II) chloride (Table 5). Bis(biguanide/substituted biguanide)copper(II) complexes persist either as genuine bis(biguanide) complexes, $[Cu(BigH)_2]^{2+}$, etc., or as mono(biguanide) complexes because of liberation of acid on the silica gel. It is well known that at a pH of about 5 bis(biguanide)copper(II) is converted into mono(biguanide)copper(II) [67]: $[Cu(BigH)_2]^{2+} + H^+ \rightleftharpoons [Cu(BigH)]^{2+} + BigH_2^+$.

As the chain length of the alkyl substituent in the BigH/AAUH increases, the R_F values of the corresponding copper(II) complexes decrease in KCl developer because of enhanced insolubility (Table 5). With K_2SO_4 as developer,

TABLE 5

R_F values of copper(II) complexes in different developers (TLC on silica gel) [17,18]

Complex	0.5 M KCl	0.5 M K_2SO_4	0.5 M $Na_2S_2O_3$	0.5 M KNa tartrate
$[Cu(BigH)_2]Cl_2$	0.66	—	1.00	0.96
$[Cu(Me\text{-}BigH)_2]Cl_2$	0.58	—	1.00	0.97
$[Cu(Et\text{-}BigH)_2]Cl_2$	0.46	—	1.00	0.96
$[Cu(Pr^i\text{-}BigH)_2]Cl_2$	0.35	—	1.00	0.98
$[Cu(Me_2\text{-}BigH)_2]Cl_2$	0.48	—	1.00	0.97
$[Cu(Et_2\text{-}BigH)_2]Cl_2$	0.52	—	1.00	0.96
$[Cu(Ph\text{-}BigH)_2]Cl_2$	0.32	—	1.00	0.90
$[Cu\{Et(BigH)_2\}]Cl_2$	0.49	—	1.00	—
$[Cu(AMUH)_2]Cl_2$	0.46	0.56	1.00	0.96
$[Cu(AEUH)_2]Cl_2$	0.37	0.40	1.00	0.95
$[Cu(AP^nUH)_2]Cl_2$	0.26	0.30	1.00	0.97
$[Cu(AP^iUH)_2]Cl_2$	0.30	0.35	1.00	0.93
$[Cu(AB^nUH)_2]Cl_2$	0.20	0.21	1.00	0.92
$[Cu(AB^iUH)_2]Cl_2$	0.22	0.25	1.00	0.91
$[Cu(AA^nUH)_2]Cl_2$	0.14	0.23	1.00	0.93
$[Cu(AA^iUH)_2]Cl_2$	0.16	0.24	1.00	0.92
$[Cu(en)_2](NO_3)_2$	0.60 (0.14)[a]	0.75 (0.33)[a]	1.00 (1.00)[a]	0.80
$[Cu(gly)_2]$	0.70 (0.13)[a]	—	[b]	0.98
$[Cu(H_2O)_6]Cl_2$	0.75	0.82	1.00	1.00

— = The spot either did not travel at all or diffused from the point of application. [a] Values in parentheses were reported by Yoneda [58]. [b] The complex was reduced by $Na_2S_2O_3$.

all biguanidecopper(II) complexes remain at the point of application because of the extreme insolubility of the bis(biguanide)copper(II) sulfate [63,65,66,68] and their greater inertness to the liberated acid than the corresponding nickel(II) complexes. However, the corresponding 1-amidino-*O*-alkylurea-copper(II) complexes travel in the same developer, again because the 1-amidino-*O*-alkylurea complexes are more susceptible to acid [63,64]. In $Na_2S_2O_3$ developer, all copper(II) complexes move to the solvent front (R_F = 1.00), possibly because of the reduction of Cu(II) to Cu(I) species, followed by the formation of anionic thiosulfatocopper(I) complexes. In KNa tartrate, all Cu(II) complexes have the same R_F values, indicating that they are not being chromatographed as genuine complexes but as some tartratocopper(II) species.

(c) Copper(II) mixed chelates

In a recent paper chromatographic study, Dutta and Ray [5] observed that [Cu(gly)(BigH)]Cl always gives two spots in all the developers studied, and they suggested that the following equilibrium is involved:

$$2[Cu(gly)(BigH)]Cl \rightleftharpoons [Cu(gly)_2] + [Cu(BigH)_2]Cl_2$$

In view of the above results, it appeared likely that the same complex would also provide two spots with aqueous KCl developer in TLC studies. The authors, however, obtained only a single spot (somewhat larger in size) than that shown by [Cu(gly)$_2$] and [Cu(BigH)$_2$]Cl$_2$, indicating that the two expected spots have fused together (R_F values: [Cu(BigH)$_2$]Cl$_2$ = 0.68; [Cu-(gly)$_2$] = 0.70; [Cu(gly)(BigH)]Cl = 0.68). Thus the above equilibrium has neither definitely been established nor eliminated in the case of [Cu(gly)-(BigH)]Cl on silica gel.

Octahedral complexes [69] of the type [Cu(X)(Y)]Cl$_2$ · nH$_2$O (X = dipy/*o*-phen; Y = BigH, etc.) exhibit zero R_F values when developed with water on a silica gel bed, suggesting that the aquo groups at the axial positions are replaced by the silanol group, thus favoring a copper—oxygen (silica gel) bond [70].

(d) Cobalt(III) complexes

In TLC studies, when cationic complexes are developed with 0.1 M salt solutions (KCl, KI, K_2SO_4, $Na_2S_2O_3$, etc.), the R_F values of the complex cations show a regular increase with the decrease of ionic charge. A reverse order of R_F values occurs when the same complexes are developed with salt solutions of higher concentration (0.2 M) [17].

In water, silica gel becomes negative, and, consequently, cationic complexes are held on the silica gel surface. As electrolytes are fed into the developer, the thirst of silica gel anions is largely quenched by the cations in the electrolyte, thereby allowing a more comfortable journey of the complex cations up the silica gel bed. A difference in R_F with cationic charge (+1> + 2> + 3) is expectedly observed but only to a certain point. If the concentration of the electrolyte in the developer is high, outer-sphere association between the complex cation and the electrolyte anions takes place, and this effect increases with increasing charge on the cation. A reversal of the order of R_F is therefore not out of order [17,18].

Tables 4 and 5 show the R_F values of several nickel(II) and copper(II) complexes of biguanide and the closely related 1-amidino-*O*-alkylurea ligands.

C. BEHAVIOR OF THE SAME METAL COMPLEXES ON DIFFERENT STATIONARY PHASES

Studies of the same complexes on filter paper and on TLC (silica gel, cellulose, alumina, etc.) should shed light on the reactions of metal complexes with different stationary phase materials, and such is found to be the case.

From different sets of experiments Yoneda et al. [11—16,43,44,58] concluded that both paper and silica gel become negative in water. Therefore adsorption of cationic complexes on the stationary phase occurs by ion exchange. However, when alumina is used as the stationary phase, neutral complexes register the highest R_F values (~0.5), and there is a gradual reduction in R_F values (for +1 charged complexes, R_F ~ 0.40; for +2, R_F = 0.2, and for +3, R_F = 0.00; for —1 and —3 charged complexes R_F = 0.00) with increase in the absolute values of the ionic charges on the complexes. Alumina is charged negatively compared to complex cations and positively compared to complex anions, possibly because of its amphoteric nature.

Kirk et al. [56] studied both cationic and anionic chromium(III) complexes using silica gel and alumina as the stationary phases and aqueous $HClO_4$—$NaCH_3COO$ as the developer. Like others, they also noticed that with the change of stationary phase but with the same developer, changes in R_F occur. Unfortunately, they could not establish any relationship between the complex, stationary phase, and composition of the developer.

Jursík et al. [38] used different adsorbents like cellulose, silica gel and alumina, and they separated Δ-*fac*(N)(*cis*) and Δ-*mer*(N)(*trans*) isomers of [Co-(S-(+)-α-alan)$_3$] with an aqueous n-propanol—n-butanol mixture. For the Δ-*fac*-(N) isomer, R_F values follow the order cellulose > silica gel > alumina, whereas for the Δ-*mer*(N) isomer, R_F is almost independent of the stationary phases.

D. ELUCIDATION OF COMPLICATED REACTIONS INVOLVING SEVERAL COMPLEX SPECIES

Glycyl-L-histidine(H_2L), $CoSO_4$, and oxygen react in the presence of water at pH 9 to give five different cobalt(III) complexes. These were separated both by anion exchange and Sephadex chromatography [71]. Of the five, three were mononuclear, viz., $[CoL_2]^-$, $[CoL(HL)]$ and $[Co(HL)_2]^+$, and the other two complexes were binuclear, viz., $[Co_2(HL)L_3]^-$ and $([Co(HL)L_2])_2$.

The compound thought to be *trans*-$[Co(dipy)_2Cl_2]Cl$ was proved by paper chromatography [71a] to be a mixture of *cis*-$[Co(dipy)_2Cl_2]^+$, $[Co(dipy)_3]^{3+}$ and $[CoCl_4]^{2-}$.

By means of electrophoresis Kauffman et al. [72] proved that yellow [Ir-$\{(C_2H_5)_2S\}_3Cl_3]$ is the *cis* (or *fac*) (1, 2, 3) neutral isomer, whereas red [Ir-$\{(C_2H_5)_2S\}_3Cl_3]$ is a red polymerization isomer, *trans*-$[Ir\{(C_2H_5)_2S\}_4Cl_2]$ *trans*-$[Ir\{(C_2H_5)_2S\}_2Cl_4]$, instead of the two expected neutral geometric isomers. More recently, by column chromatography Kauffman et al. [40] completely separated the two forms. The red form, being an electrolyte, is adsorbed more strongly on the silica gel bed than the neutral *cis* isomer.

Fogel et al. [73] studied the behavior of the chromium(III) sulfate system. After dissolving $Cr_2(SO_4)_3$ in dilute H_2SO_4 of various concentrations, they separated the $[Cr(SO_4)_2]^-$ anion from other species by cation exchange. They claimed that the SO_4^{2-} groups function as bidentate ligands in this species despite previous workers' claims [74] of monodentate behavior on the basis of infrared and solid state studies.

Ćelap et al. [75] isolated four geometric isomers of the dinitrobis(glycinato)-cobaltate(III) anion, and more recently they [76] investigated the isomerization kinetics of these complexes at various temperatures by paper chromatography using dioxane—water with NaI as the developer. They proposed the following mechanism:

$$\begin{tikzcd}
\mathrm{I} \arrow[r, "k_1"] & \mathrm{II} \arrow[rr, "k_4"] \arrow[dr, shift left, "k_2"] & & \mathrm{IV} \\
& & \mathrm{III} \arrow[ul, shift left, "k_3"] \arrow[ur, "k_5"'] &
\end{tikzcd}$$

where I = *cis*-NO_2|*cis*-N|*cis*-O, II = *trans*-NO_2|*cis*-N|*cis*-O, III = *trans*-NO_2|*trans*-N|*trans*-O, IV = *cis*-NO_2|*trans*-N|*cis*-O, of the same complex, $[Co(gly)_2(NO_2)_2]^-$.

E. PREDICTION OF THE EXISTENCE OF NEW METAL COMPLEXES

Chromatographic techniques have often revealed the existence of compounds in solution whose existence was not previously suspected. The cationic species present in boiled aqueous solutions of chromium(III) perchlorate were separated by ion exchange chromatography, which revealed the presence of two new species [71] (perhaps polymers) in addition to the $[Cr(H_2O)_6]^{3+}$ ions.

Preobrazhenskiĭ and Lilova [77] separated mixtures of aquochlorochromium(III) by cation-exchange column chromatography. They identified a new species as $[Cr(H_2O)_3Cl_3]$, which neither dissociates to give ions nor is adsorbed on the resin bed (cationic or anionic). This was not detected by other techniques because it is quickly converted to other species.

In a paper chromatographic study Hill-Cottingham [78] observed that when EDHPA—iron(III) is developed with butanol, it shows two components, indicating that the iron(III) compound exists in two forms. Ryskiewich and Boka [79] confirmed that iron(III) exists in meso and racemate forms.

Zompa [80] prepared and isolated three geometric isomers of the bis(histidinato)cobalt(III) ion by ion exchange chromatography. Ardon and Herman [81] obtained from a reddish brown solution a new reddish brown compound $[Cr(H_2O)_5(NO)]^{2+}$, which was separated from the accompanying green binuclear $[Cr_2O]^{4+}$ ion and the greyish blue $[Cr(H_2O)_6]^{3+}$ ion by elution with $HClO_4$ through a cation exchange column.

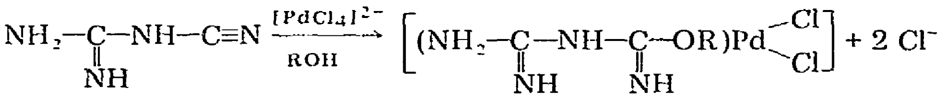
The previously uncharacterized aquopentachloroosmate(IV) ion was obtained similarly in solution from a $[OsCl_6]^{2-}$ aquation mixture by ion exchange [82].

The behavior of histidinatocopper(II) in the presence of copper(II) lysinate was studied electrophoretically by Wieland and Fischer [83]. In their separation they noticed a third spot which they considered to be a mixed complex of copper, e.g., histidinatolysinatocopper(II).

Hughes and Garner [84] allowed $[Cr(en)(NH_3)(O_2)_2] \cdot H_2O$ to react with HBr and obtained a crude product, which, after elution through a cation exchange column with $HClO_4$, provided a new complex $[Cr(en)(NH_3)(H_2O)Br_2]^+$.

In a limited number of cases paper chromatography has indicated the possible existence of hitherto unknown complexes. For example, in a chromatographic study Dutta and Ray [7] noticed that $[Pd(AMUH)_2]Cl_2$ forms two distinct spots in aqueous KCl containing pyridine as the developer. This result was rather unusual since the very similar $[Pd(BigH)_2]Cl_2$ forms only a single distinct spot in the same developer. This unusual chromatographic behavior led them to suggest the following possible equilibrium: $[Pd(AMUH)_2]Cl_2 \rightleftharpoons [Pd(AMUH)Cl_2] + AMUH$.

A high concentration of chloride ion in the developer possibly facilitates the shifting of the equilibrium towards the mono(1-amidino-*O*-alkylurea) derivative. Dutta and Ray [7] also verified that the spot with the higher R_F value is not due to the $[PdCl_4]^{2-}$ anion or to $[Pd(Py)_2Cl_2]$, both of which give R_F values almost close to the solvent front, but is due to $[Pd(AMUH)Cl_2]$. This is what one would expect from considerations of charge. This conclusion was verified from an independent synthesis of the complex by two routes: (1) addition of alcohol to dicyandiamide in the presence of palladium(II) ion, and (2) by reaction of $[PdCl_4]^{2-}$ with AMUH · HCl at pH 3.



$$\mathrm{NH_2{-}\underset{\underset{NH}{\|}}{C}{-}NH{-}C{\equiv}N} \xrightarrow[\mathrm{ROH}]{[\mathrm{PdCl_4}]^{2-}} \left[(\mathrm{NH_2{-}\underset{\underset{NH}{\|}}{C}{-}NH{-}\underset{\underset{NH}{\|}}{C}{-}OR)Pd}\genfrac{}{}{0pt}{}{\mathrm{Cl}}{\mathrm{Cl}}\right] + 2\,\mathrm{Cl^-}$$

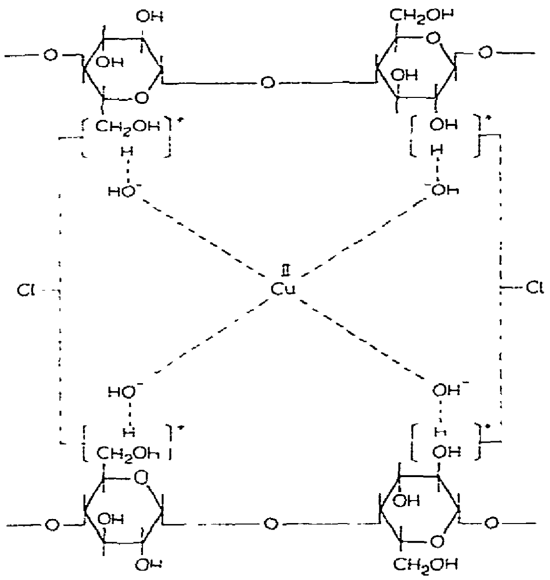
(Dicyandiamide)

These independently synthesized complexes provided the same higher R_F value as was obtained from $[Pd(AMUH)_2]Cl_2$.

F. FILTER PAPER CHROMATOGRAPHY

(i) A suggested mechanism

Despite numerous studies by various workers, the actual mechanism of filter paper chromatography is not yet well understood. This mechanism may



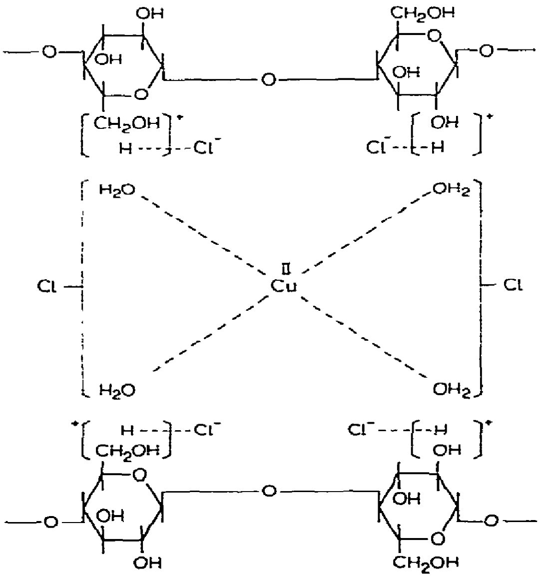


Fig. 1. The mode of adsorption of the Cu^{2+} aquo complex on cellulose.

Fig. 2. The mode of desorption of the Cu^{2+} aquo complex in the presence of H^+ ions.

be considred as (1) adsorption of the metal ions by the cellulose molecules of the filter paper (Fig. 1), (2) desorption of the adsorbed metal ions by acids (Fig. 2) and (3) migration of the metal ions due to solvation [85—91].

Paul and Janardhan [88] found no linear relationship between R_F values of a particular metal ion and the surface tension, viscosity or dielectric constant considered individually, but they did find that R_F values vary linearly with the dielectric constant/viscosity quotient. However, a coordination chemist is more interested in finding out how the R_F values of a series of closely related complexes vary in a given developer and a given stationary phase.

(ii) Amino acid complexes of some dipositive metal ions

Using aqueous ethanol or n-propanol as the mobile phase and paper as the stationary phase, Jursík [2] found that R_F values for bis(glycinato)metal(II) (Cu(II), Ni(II), Zn(II) and Cd(II)) have the following order: Ni > Cu > Cd > Zn, which corresponds to the decreasing ionic radius of the central atom. The lower R_F value for the zinc(II) complex is possibly connected with the dissociation of the complex in the developer solvent.

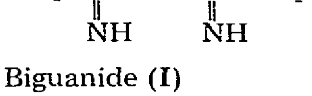
Jursík [3] tried to separate the *cis* and *trans* isomers of bis(glycinato)-copper(II) by using mixed solvents (H_2O—CH_3OH; H_2O—C_2H_5OH; H_2O—C_3H_7OH; H_2O—CH_3COCH_3, etc.) as the developer. He claimed that the *cis* isomer has greater R_F values than the corresponding *trans* isomer. To him the difference of R_F is not related to the difference in dipole moments but possibly to steric hindrance or to the different adsorptivity of both isomers.

(iii) Attempts to correlate charge with R_F

Using 1 M ethylamine as the developer, Yoneda [11], and later Bag and Syamal [93], were able to categorize cobalt(III) complexes of different charge types (+3 to —3) on the basis of R_F values. The highest R_F values were observed for anionic and neutral complexes, while the lowest R_F values were observed for tripositive cations. Thus mobility of the complexes can be related to their charge. It has been our experience that categorization of charges of complexes on the basis of R_F alone is not always a reliable guide [17].

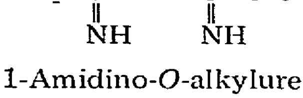
(iv) Some recent studies of square planar copper(II), nickel(II) and palladium-(II) complexes of biguanide and 1-amidino-O-alkylureas

A number of square planar copper(II), nickel(II) and palladium(II) complexes of a variety of substituted biguanide(I) and 1-amidino-*O*-alkylurea(II) have been studied, along with a host of substitution-inert cobalt(III) homochelates and heterochelates.



$$\mathrm{NH_2{-}\underset{\underset{NH}{\|}}{C}{-}NH{-}\underset{\underset{NH}{\|}}{C}{-}NH_2}$$

Biguanide (I)



$$\mathrm{NH_2{-}\underset{\underset{NH}{\|}}{C}{-}NH{-}\underset{\underset{NH}{\|}}{C}{-}OR}$$

1-Amidino-*O*-alkylurea(II)

(a) Nickel(II) and copper(II) biguanide complexes

Since metal biguanide complexes are stable to dissociation at pH ~7, Dutta and Ray selected those salts which may quench the undesirable effect of the cellulose anion in maintaining the pH at about 7. Satisfactory spots were obtained by using either aqueous ammonium acetate or aqueous KCl containing pyridine [4—6]. Although ammonium acetate solution produces a pH (ca. 6.5—6.8) at which metal(II) biguanide complexes should not dissociate, its use was abandoned since spectrophotometric studies revealed that the electronic spectra of copper(II), nickel(II) and palladium(II) complexes had undergone substantial modification. However, aqueous KCl—pyridine developer produces the same electronic spectra for the complexes as these complexes exhibit in aqueous solution [4—6,17].

(b) Effect of KCl—pyridine

Variation of KCl concentration in aqueous pyridine revealed that R_F values of all complexes increase with increasing KCl concentration. It is to be noted that neither KCl nor pyridine alone can give good spots but a suitable combination of the two does. Pyridine substantially increases the solubilities of the complexes.

Interestingly, raising the pyridine concentration and lowering the KCl concentration yields two spots with $[Cu(BigH)_2]Cl_2$. Dutta and Ray [4] established the following equilibrium: $[Cu(BigH)_2]Cl_2 + 4\ Py \rightleftharpoons [Cu(Py)_4]Cl_2 + 2\ BigH$. A new spot appears due to $[Cu(Py)_4]Cl_2$, which was verified by independent experiments on $CuCl_2$ in the KCl—pyridine mobile phase. The corresponding nickel(II) complexes do not show two spots although the sizes of the spots are very large. Palladium(II) complexes exhibit only one spot, which is evidence for the preponderance of only one species.

TABLE 6

Solubility and R_F values of bis(biguanide/substituted biguanide)copper(II) complexes (Developer: 100 ml 0.5 M KCl + 5 ml pyridine)

Complex	Solubility (in g/100 ml of developer)	R_F
$[Cu(BigH)_2]Cl_2$	20.84	0.46
$[Cu(Me\text{-}BigH)_2]Cl_2$	7.96	0.52
$[Cu(Et\text{-}BigH)_2]Cl_2$	0.45	0.64
$[Cu(Pr^i\text{-}BigH)_2]Cl_2$	0.22	0.66
$[Cu(Me_2\text{-}BigH)_2]Cl_2$	0.32	0.72
$[Cu(Et_2\text{-}BigH)_2]Cl_2$	0.33	0.78
$[Cu\{Et(BigH)_2\}]Cl_2$	0.31	0.46
$[Cu\{Et(BigH)_2\}]Cl_2$	0.48	0.44
$[Ni\{Et(BigH)_2\}]Cl_2$	0.24	0.30

(c) Effect of size of the complex on R_F values

The increase of R_F in the order Pd << Cu < Ni corresponds to the decreasing size and molecular weight of the complexes Pd > Cu > Ni. However, a reverse order of R_F, e.g., $[\mathrm{Cu\{Et(BigH)_2\}}]^{2+} > [\mathrm{Ni\{Et(BigH)_2\}}]^{2+}$, is observed, which was explained on the basis of the higher solubility of the copper(II) complexes compared to the corresponding nickel(II) complexes (Table 6).

(d) Effect of substitution on R_F values

On increasing the alkyl substitution on the N^1 atom of biguanide, the R_F values of the corresponding copper(II), nickel(II) and palladium(II) bis-(biguanide) complexes also increase [4]. However, phenyl substitution lowers the R_F values [4]. Since biguanide and alkyl biguanide have more or less similar basic character, it is a reasonable guess that the attractive influence of the dipositive cations on the cellulose anion will be quite similar. However, substitution of the H atom attached to the N^1 atom of the biguanide considerably reduces the chances of forming H-bonded species with cellulose anions. This is expected to lead to higher R_F values with increasing substitution. Had solubility alone been responsible for the difference in R_F values, a reverse order of R_F values would have occurred. In fact, experimental determination of the solubility of metal biguanides shows the order [6]: $[\mathrm{M(BigH)_2}]\mathrm{Cl_2} >> [\mathrm{M(Me{-}BigH)_2}]\mathrm{Cl_2} > [\mathrm{M(Et{-}BigH)_2}]\mathrm{Cl_2} > [\mathrm{M(Ph{-}BigH)_2}]\mathrm{Cl_2} > [\mathrm{M(Pr{-}BigH)_2}]\mathrm{Cl_2} > [\mathrm{M(Me_2{-}BigH)_2}]\mathrm{Cl_2} > [\mathrm{M(Et_2{-}BigH)_2}]\mathrm{Cl_2}$ (where M = Cu or Ni) (Tables 6 and 7).

Increase in R_F values from biguanide to methyl biguanide and then to other alkyl-substituted biguanides is also likely to be related to the inductive

TABLE 7

Solubility and R_F values of bis(1-amidino-*O*-alkylurea)metal(II) complexes (Developer: 100 ml 1 M KCl + 5 ml pyridine)

Complex	Solubility (in g/100 ml of developer)	R_F
$[\mathrm{Ni(AMUH)_2}]\mathrm{Cl_2}$	0.26	0.85
$[\mathrm{Ni(AEUH)_2}]\mathrm{Cl_2}$	1.19	0.86
$[\mathrm{Ni(AP^nUH)_2}]\mathrm{Cl_2}$	0.62	0.86
$[\mathrm{Ni(AP^iUH)_2}]\mathrm{Cl_2}$	0.82	0.86
$[\mathrm{Ni(AB^nUH)_2}]\mathrm{Cl_2}$	0.34	0.84
$[\mathrm{Ni(AB^iUH)_2}]\mathrm{Cl_2}$	0.36	0.83
$[\mathrm{Ni(AA^nUH)_2}]\mathrm{Cl_2}$	0.30	0.73
$[\mathrm{Ni(AA^iUH)_2}]\mathrm{Cl_2}$	0.30	0.73
$[\mathrm{Cu(AMUH)_2}]\mathrm{Cl_2}$	0.05	0.67
$[\mathrm{Cu(AEUH)_2}]\mathrm{Cl_2}$	0.069	0.71
$[\mathrm{Cu(AP^nUH)_2}]\mathrm{Cl_2}$	0.338	0.74
$[\mathrm{Cu(AP^iUH)_2}]\mathrm{Cl_2}$	1.244	0.84
$[\mathrm{Cu(AB^nUH)_2}]\mathrm{Cl_2}$	0.449	0.69
$[\mathrm{Cu(AB^iUH)_2}]\mathrm{Cl_2}$	0.309	0.69

influence of the electron-releasing alkyl groups whereby the overall charge on the complex cation may be diminished to some extent. This lowering of charge will enhance the R_F values. On the contrary, electron-withdrawing phenyl substitution leads to lower R_F values.

In the case of 1-amidino-*O*-alkylurea complexes, the H-bond formation remains invariant throughout the series because alkyl substitution in the OR moiety does not lead to any decrease of H atoms in the ligand backbone. On the other hand, alkyl substitution of the N^1 atom of biguanide does lead to a decrease of the available H atoms, but the inductive effect of the alkyl groups remains. Dutta and Ray [6] strongly believed that solubility plays a greater role here since the solubility of copper(II) complexes in aqueous KCl—pyridine developer is found to increase with increasing chain length of the alkyl substituent (from methyl to isopropyl) (Tables 6 and 7).

(v) Behavior of some homochelates and mixed chelates of cobalt(III) and copper(II)

(a) Cobalt(III) mixed chelates

In describing paper chromatographic results, Yoneda [11] made a passing reference to the fact that R_F values of $[Co(NH_3)_6]Cl_3$ ($R_F = 0.90$) remain unchanged in 1 N electrolyte (e.g., HCl, NaCl, KBr, $NaNO_3$, $NaClO_4$, K_2SO_4). Dutta and Ray [17,18] studied $[Co(NH_3)_6]Cl_3$ and twenty-one other cobalt(III) complexes in several electrolytes (KCl, KI, K_2SO_4, $Na_2S_2O_3$ and KNa tartrate) of different charges. The variation in the R_F values indicates outer-sphere association between these complex cations and the developer electrolytes. Investigation [92] of the outer-sphere association constants of $[Co(NH_3)_6]^{3+}$, $[Co(en)_3]^{3+}$, $[Co(BigH)_3]^{3+}$ and $[Co(dipy/o\text{-}phen)(BigH)_2]^{3+}$ has shown that association constants obey the following order: $I^- < Br^- < Cl^- << SO_4^{2-}$; the larger the association constant, the larger the R_F values.

(b) Copper(II) mixed chelates

With higher concentrations of pyridine and lower concentrations of KCl, the homochelate $[Cu(BigH)_2]Cl_2$ exhibits two spots because of an equilibrium of the type: $[Cu(BigH)_2]Cl_2 + 4\ Py \rightleftharpoons [Cu(Py)_4]Cl_2 + 2\ BigH$. Interestingly, the mixed chelate $[Cu(gly)(BigH)]Cl$ yields double spots when water is used as the developer because of the following equilibrium: $2[Cu(gly)(BigH)]Cl \rightleftharpoons [Cu(gly)_2] + [Cu(BigH)_2]Cl_2$. One would therefore expect three spots from $[Cu(gly)(BigH)]Cl$ in the developer containing higher concentrations of pyridine and lower concentrations of KCl, resulting from a secondary equilibrium of $[Cu(BigH)_2]Cl_2$ with excess pyridine, i.e.,

$$\begin{tikzcd}[column sep=small]
2[Cu(gly)(BigH)]Cl \arrow[r, phantom, "\rightleftharpoons"] & {[Cu(gly)_2] +} & {[Cu(BigH)_2]Cl_2} \arrow[d, shift left, "Py"] \\
& & {[Cu(py)_4]Cl_2 + 2\ BigH} \arrow[u, shift left]
\end{tikzcd}$$

However, Dutta and Ray [5] obtained two spots instead of three, because the R_F values of $[Cu(gly)_2]$ ($R_F = 0.93$) and $[Cu(Py)_4]Cl_2$ ($R_F = 0.88$) are identical in spite of their charge difference. Thus the secondary equilibrium has neither been definitely established nor eliminated.

Copper(II) mixed chelates of the type [Cu(X)(BigH)]Cl (HX = glyH, α-alanH, o-phen) always give two spots in all the developers tried and the first type of equilibrium was suggested. However, such a disproportionation reaction is less favored in the case of [Cu(gly)(dipy)]Cl. With the proper choice of developer, $[Cu(X)(BigH)]Cl_2$ (X = dipy/o-phen) has yielded a single spot.

It has been concluded that a good single spot can be obtained with a mixed chelate only when its tendency to disproportionation into the two component homochelates is not too large and when a correct choice has been made of a developer of the stationary phase (compare paper and TLC) which can suppress the disproportionation reaction. We wish to emphasize that obtaining two spots from a mixed chelate cannot immediately be interpreted to mean that the mixed chelate is not a pure species. Two spots may mean that there is an equilibrium between the mixed chelate and the component homochelates in the developer solution and that continued development merely helps the separation of the two homochelates.

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