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CHROMATOGRAPHY OF COORDINATION COMPLEXES

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A. INTRODUCTION

Although chromatography in its many forms has been applied mostly to the separation of organic and biological materials, recent years have seen a growing number of applications of the various chromatographic techniques to inorganic separations. Not only has chromatography been used for the qualitative and quantitative analysis of inorganic substances, but it has also been employed to prepare pure inorganic compounds, to follow inorganic reaction kinetics, and to determine such physical parameters as the configuration and charge of inorganic species. It

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is in these latter areas of investigation that chromatography has been particularly useful to the coordination chemist. For the separation of ionic species, ion exchange chromatography has of course been the preferred technique. Yet the literature contains numerous examples of the separation of inorganic complexes by column, paper, thin-layer, and gas chromatography as well as by ion electrophoresis.

Most of the chromatographic separations of complexes have involved hexacoordinate octahedral species, but a few studies of tetracoordinate square planar complexes have been made[39,69,71]. The following generalizations should be valid for all coordination numbers and configurations.

The type of separation to be effected largely determines the choice of technique. For example, in cases in which the preparation or isolation of a chemical species is the goal, a column, with its greater capacity, is generally preferred. However, for the qualitative identification of components in a mixture or for the study of properties such as charge or geometry, paper, gas, or thin-layer chromatography, techniques which are rapid and adaptable to micro amounts of sample, are often more attractive.

The type of species to be separated also influences the choice of chromatographic method, adsorbent, and solvent system. Most frequently, the separation involves ions of different charge density so that use of ion exchange resins with an aqueous solvent system is most effective. Differences in retention by the resin can then be related to the charge density or charge distribution of the ions or to the ease of complex formation with the eluent*.

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* We must note here that in addition to the conventional ion exchange resins, certain other adsorbents such as silica gel and alumina should probably be classified as ion exchange types of solid substrates, at least as far as inorganic separations are concerned. A number of studies have been made of the adsorption of complex ions on silica gel[128], and considerable evidence has accumulated that silica gel can behave as a weak cation exchange resin. The gel surface consists of silanol (Si–O–H) sites whose hydrogen atoms may be exchanged for cations in a reasonably predictable manner. Dugger *et al.*[41] have tabulated enthalpy, entropy, and free energy values for the exchange reaction between metal ions and the hydrogen atom of the silanol group of silica gel. They found that the bond energy was roughly proportional to the charge density of the unhydrated ion. This finding suggests that in the chromatography of cations, those of higher charge density should be retained more strongly and so have lower R_F values. The results of a thin-layer chromatographic investigation of some inorganic ions by Druding[38] do not entirely agree with this prediction, but they do suggest that retention is at least proportional to the charge density of the hydrated ion. In the separation of alkali metal ions and alkaline earth metal ions on silica gel in an acidic solvent, the order of R_F values was $Li^+ > Na^+ > Rb^+ > Cs^+$ and $Be^{2+} > Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$.

An alternative explanation for Druding's results can be based on the ease of substitution of a silanol group for the water of hydration in the inner coordination sphere of the metal ion. Lithium, with its high charge density, would be the least likely to release its waters of hydration for a silanol group and so should exhibit less retention and consequently a higher R_F value than the other alkali metal ions.

Additional evidence for an ion exchange reaction mechanism, which is very close to the explanation just cited for the alkali metal ions was developed by Burwell *et al.*[20] in studies of the adsorption of coordination complexes on silica gel and their reaction with the gel. They found

In the choice of stationary phase and solvent, the separation of nonionic inorganic complexes may be treated in the same manner as the separation of polar organic compounds. Differences in dipole moment or solubility in the developer are the important factors that govern the effectiveness of the separation.

An exciting recent development is the use of gas chromatography for the separation of volatile nonionic metal compounds such as carbonyls, alkoxides, alkyls, and especially chelates with oxygen, sulfur, selenium, phosphorus, and nitrogen as donor atoms[112]. Since its inception in the late nineteen-fifties the application of gas chromatography to the metal chelates of the β-diketones has developed rapidly. The first such studies resulted in the separation of beryllium, aluminum, and chromium by gas chromatography of their acetylacetonates[8,54]. The method has since been extended not only to acetylacetonates of other metals but also to trifluoroacetylacetonates, hexafluoroacetylacetonates, and other ligands. By use of the new technique, rare earths[43] and geometric isomers have been separated, and even optical isomers have been resolved[139]. Further details and applications can be found in the excellent monograph by Moshier and Sievers[112].

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that the silanol group could displace chloride ion from the coordination sphere of such inert complexes as *cis*- and *trans*-$[Co(en)_2Cl_2]^+$ when these complexes were adsorbed onto the surface of the silica gel. The degree of adsorption was also found to be dependent upon the charge and charge distribution of the complex ion. Their observations were confirmed by the thin-layer chromatographic studies of some cobalt(III) complexes made by Druding and Hagel[39]. The retention values of Burwell *et al.*[20] and the R_F values of Druding and Hagel[39] for appropriate cobalt(III) ammine complexes are compared in Table 1. The greater retention of the *cis* isomers over the corresponding *trans* isomers agrees with the greater charge polarization of the *cis* complex as compared to the *trans* complex.

TABLE 1

RETENTION OF OCTAHEDRAL COORDINATION COMPLEXES ON SILICA GEL AS A FUNCTION OF CHARGE ON THE COMPLEX

Complex	*Retention (Burwell et al.)*[20]	R_F *(Druding and Hagel)*[39]
$[Co(NH_3)_6]^{3+}$	—	0.20
$[Co(NH_3)_5NO_2]^{2+}$	0.036 mole/g.SiO_2	0.23
cis-$[Co(NH_3)_4(NO_2)_2]^+$	—	0.60
trans-$[Co(NH_3)_4(NO_2)_2]^+$	—	0.80
$[Co(NH_3)_3(NO_2)_3]$	slight	0.98
$[Co(NO_2)_6]^{3-}$	no retention	1.00

In his study of the paper chromatography of cobalt(III) amines, Yoneda[158] suggests that even on cellulose, an ion exchange mechanism may be the basis for separation. In the absence of an electrolyte in the developer, long tails and diffuse spots resulted. However, with an electrolyte in the developer, tailing decreased; the spots were more intense, but some tailing persisted. Use of a base eliminated the tailing. Yoneda cites this as evidence for an ion exchange mechanism involving the hydroxy sites of the cellulose structure. The electrolyte displaces the complex ion from the cellulose. As the value of the charge on the complex decreases, its mobility increases. Yoneda[158] has even suggested the possibility of determining the ionic charge on a complex by noting its R_F value.

We shall now briefly review recent developments in the chromatography of coordination complexes according to the type of separation involved. The coverage is intended to be illustrative rather than exhaustive.

B. SEPARATION AND IDENTIFICATION OF DIFFERENT ELEMENTS BY FORMATION OF COORDINATION COMPLEXES

In this phase of chromatography, *viz.*, the separation and identification of different metal ions by complex formation with the same ligand, the formation of the complex ion is only the means for effecting the separation of the elements[53].

In some cases complex formation is mandatory; *e.g.*, amphoteric elements such as arsenic and antimony, which hydrolyze completely and immediately on an alumina column, can be chromatographed as tartrate complexes[132]. The order of elution of species can also be changed by conversion to complexes[132].

Several months after the first articles[1,93] on the paper chromatography of cations had appeared, Elbeih *et al.*[44] pointed out that the formation of complexes plays an important role in the separation of cations. R_F values have been correlated with stability constants of complexes[73,74].

As might be expected, ion exchange methods, with their high sensitivities to slight differences in charge densities, have been the most popular of chromatographic separations. Only a few of the more recent separations of unusual complexes will now be cited. Chromatographic separation of elements by complex formation is almost as old as the invention of modern ion exchange resins. The now classical separation of iron, cobalt, and nickel depends on the formation of hexachloro complexes of each ion under various conditions. Kurt A. Kraus and his co-workers have made extensive studies of the separation of many elements as chloro complexes by means of anion exchange resins[83]. Commercial separation of the lanthanide elements from one another is usually accomplished on cation exchange columns; formation and stability of the lanthanide-EDTA complex are the dominant equilibria here[70].

In a few instances such as those just cited, where either a preparation is involved or a subsequent quantitative determination of each species is desired, column methods are preferred because of their greater capacity. Usually, however, the purposes of separating individual elements is to identify rapidly and qualitatively the components of a mixture. In such cases, a method more suitable to semimicro or micro quantities is then used (paper, gas, or thin-layer chromatography or ion electrochromatography).

Table 2 lists a few recent separations of different elements as coordination complexes. In most of these separations, the mechanism of separation can be correlated with the charge density of the complex species or with the difference in

TABLE 2

SEPARATION OF ELEMENTS BY FORMATION OF COORDINATION COMPLEXES

Elements separated	*Ligand*	*Chromatographic medium*	*Ref.*
Various elements	chloride ion	column; Dowex 1	83
Cd, Cu, Ni, Zn	glycinate ion	paper	63
Ca, Cu	ammonia	column; alumina	81
Hg, Cu, Cd, Bi, Pb	diethyldithiocarbamate ion	thin-layer; silica gel	136
Zn, Cd	pyridine, thiocyanate ion	paper	146
Lanthanides	bis(2-ethylhexyl)phosphate ion	thin-layer; silica gel	36, 105
Lanthanides	α-hydroxybutyric acid	thin-layer cellulose electrophoresis	3, 17
Cr, Co	ammonia	column; silica gel	61
Cu-Cd, Th-Fe-UO_2^{2+}, Th-Ce-Fe, Al-Zr, Ti-Fe-Al	chloride ion	ion exchange–impregnated paper	94
Transition metals	fluoride ion	ion exchange–impregnated paper	95
Ni, Co, Mn, Zn, Sb, Sn, Al, Cr	ammonia, hydroxide ion	ion electrophoresis	103
Fe, Co, Mn, Ni	nitrosonaphthol	thin-layer; silica gel	137
Cu, Ni, Co	thiocyanate ion	paper	145
Ni, Co, Cd, Cu, Zn	thiocyanate ion	thin-layer; silica gel	147
Ag, Zn, Cu, Cd, Co	ethylenediamine	thin-layer; silica gel	151
Co from Cu, Tl, Zn, Ni	ethylenediaminetetra-acetate ion	column; silica gel	149
Zn, Cu	citrate ion	column; silica gel	150
Ag, Au, Pd, Pt	dithizone	thin-layer; silica gel	57
Hg, Pb, Cu, Bi, Cd, Zn	dithizone	thin-layer; silica gel	56
Cu, Cd, Hg, Pb, Bi	dithizone	paper	113, 114
Be, Al, Cr	acetylacetone	gas chromatography	8, 54
Lanthanides	2,2,6,6-tetramethyl-3,5-heptanedione	gas chromatography (Teflon, 2% Apiezon H on Gas Pack F)	43

stability of the complex ion itself with respect to substitution or solvolysis. In Lederer's work[94–96] with ion exchange-impregnated paper, separation is based on differences in the formation of either chloro or fluoro complexes of the metal ions with the solvent, resulting in desorption from the cation exchanger. Kolthoff and Stenger's separation[81] of copper from calcium depends upon the formation of the copper(II) ammine complex, which has a lower charge density than does the calcium ion. On the other hand, Jursík's separation of some post-transition metal bisglycinates[63] is related entirely to the charge densities of these complexes.

C. PREPARATION AND PURIFICATION OF COORDINATION COMPLEXES

With increasing frequency, the inorganic chemist is turning to the use of chromatography in his attempts to prepare and purify isomerically pure coordination complexes. Chromatography is usually applied to separate the product from its reactants, but in many cases a separation of the product from possible by-products is also desired. Ion exchange methods have been the almost universal choice for preparative work because of the capacity of columns for preparative quantities of material and because of the ionic nature of the substances to be separated. Usually, the product is of quite different charge density from the reactants (starting materials for the most common preparations of coordination complexes are hydrated metal cations and either neutral or anionic ligands).

Although preparative thin-layer chromatography has been extensively applied to the preparation and isolation of small quantities of valuable organic and biochemical substances and although Kauffman and Benson[69] have demonstrated the feasibility of preparative separations of inorganic complexes by TLC, no applications of preparative thin-layer chromatography to coordination compounds have been reported. This technique would be of greatest advantage in cases where

TABLE 3

USE OF CHROMATOGRAPHY IN THE PREPARATION AND PURIFICATION OF COORDINATION COMPLEXES

Product	*Other components*	*Stationary phase*	*Ref.*
Substituted acetylacetonates of Co^{III} and Cr^{III}	HAcac[a], Co^{3+}, Cr^{3+}	column; alumina	31
Metal trifluoroacetylacetonates	metal benzoylacetonates	column; alumina	48
$[Co(Acac)_3]$[a]	reaction by-products	column; Florosil	31
$[Co(NH_3)_4Cl_2]^+$	$[Co(NH_3)_4(H_2O)Cl]^{2+}$	ion electrophoresis	124
$[Co(H_2O)(Acac)_2NO_2]$	other ions	column; Dowex 1	35
$[Co(en)_2am]^{2+}$[b]	amino acids (Ham)	paper; thin-layer; cellulose	18
$[(H_2O)_4Cr(OH)(SO_4)Cr(H_2O)_4]^{3+}$	$[Cr(H_2O)_6]^{3+}$, OH^-	column; Dowex 50	50a
Bis(2,3-diaminopropionato)cobalt(III) chloride	$Na_3[Co(CO_3)_3]$, 2,3-diaminopropionic acid hydrochloride	column; Dowex 50	50b
$[Co(trien)am]^{2+}$[c]	amino acids(Ham)	paper; thin-layer; cellulose	19
Nitro-en-pn complexes of Co^{III}	$[Co(NH_3)(en)(NO_2)_3]$, pn	paper	65
$[Co(gly)_2(L\text{-}val)]$[d]	amino acids, Co complexes	column; alumina	138
Co^{III} amines	anions	column; Amberlite IRA 140	2
$[Cr(H_2O)_6]^{3+}$	$[Cr(H_2O)_5(NCS)]^{2+}$, $[Cr(H_2O)_4(NCS)_2]^+$	column; Dowex 50	76
$[Cr(NH_3)_6]^{3+}$	$[Cr(NH_3)_5(H_2O)]^{3+}$, $[Cr(NH_3)_4(H_2O)_2]^{3+}$	column; alumina	62
$[Cr(en)(H_2O)_4]^{3+}$	$[Cr(H_2O)_6]^{3+}$	column; Dowex 50	27a
$[Cr(en)_2(H_2O)Cl]^{2+}$	$[Cr(en)_2Cl_2]^+$	column; Dowex 50	100
$Cr(en)_2(H_2O)Cl]^{2+}$	other ions	column; Dowex 50	101
$[Cr(en)_2F_2]^+$	$[Cr(en)_2(H_2O)F]^{2+}$	column; Dowex 50	49, 142a
$[Cr(en)_2(H_2O)NCS]^{2+}$	$[Cr(en)_2(NCS)Cl]^+$	column; Dowex 50	144
$[Cr(H_2O)_5I]^{2+}$	reactants	column; Dowex 50	117
Troponeiron carbonyls	iron carbonyls	column; alumina	14

TABLE 3 *(continued)*

Product	*Other components*	*Stationary phase*	*Ref.*
Organometallic carbonyl complexes of cobalt	acetylenes and cobalt compounds	column; alumina	86, 87
Organometallic carbonyl complexes of iron	acetylene and iron carbonyls	column; alumina	153
cis-$[Rh(C_5H_5N)_3Cl_3]$	*trans*-$[Rh(C_5H_5N)_4Cl_2]Cl$	column; alumina	131
$[Ru(H_2O)_3Cl_3]$	other Ru^{III} complexes	column; Dowex 50W, Dowex 1	34
$[Ru(H_2O)_2Cl_4]^-$	other Ru^{III} complexes	column; Dowex 1	15
$[Pd(Acac)_2]$	reaction products	column; alumina	142
Alkyl and aryl derivatives of Pt^{II} phosphines	starting materials and isomers	column; alumina	26, 27
$C_5H_5Fe(CO)(COCH_3)L$ $(L = (C_6H_5)_3P, (C_4H_9)_3P, (C_4H_9O)_3P)$	$C_5H_5Fe(CO)_2CH_3$ and phosphines or phosphites	column; alumina	7
$Rh_2[(C_6H_5O)_3P]_4(SCN)_2$	$Rh[(C_6H_5O)_3P]_2COCl$, KSCN	column; alumina	60
$[Mo(CO)_4\text{-}\{(C_6H_5)_3M\}SCN]$ (M = P, As, Sb)	*cis*-$[Mo(CO)_3\{(C_6H_5)_3M\}_2SCN]$, *trans*-$[Mo(CO)_3\text{-}\{(C_6H_5)_3M\}_2NCS]$	column; alumina	155
Thiocyanatocarbonyl Mn^I complexes	Thiocyanatopentacarbonylmanganese(I), amines, phosphines, arsines, stibines	column; Florosil, alumina	45
$[Co(fac)_3]$[e]	$Co_2(CO)_8$, hfac	column; alumina	75
$[CH_3SFe_2(CO)_6]_2S$	$Fe_3(CO)_{12}$, $[CH_3SFe(CO)_3]_2$, methyl thiocyanate	column; alumina	28
$[(CH_3S)_2Fe_2(CO)_4C_7H_8]$	*anti-* and *syn*-$[CH_2SFe(CO)_3]_2$	column; alumina	80
Fulveneiron carbonyls	fulvenes and iron carbonyls	column; alumina	152
$[MCl_nBr_{6-n}]^{2-}$ (M = Ir, Os, Pt, Re; n = 0, 1, ... 6)	M^{IV}, Cl^-, Br^-	paper; high voltage electrophoresis	12, 120–122
Chloroaquo and chlorohydroxo complexes of Rh^{III}, Ir^{III} and Pt^{IV}	Rh^{III}, Ir^{III}, Pt^{IV}, Cl^-, OH^-	paper; high voltage electrophoresis	11
L-β-[Co(trien)Ox]Cl[f]	L-β-$Co(trien)Cl_2]Cl$, H_2Ox, K_2Ox	column; Dowex 50	92
$[Co(en)(gly)_2]^+$	$CoCl_2$, en, glycine	column; Dowex 50	106
$[Co(gly)_2Ox]^-$	$CoCl_2$, glycine, Ox^-	column; Dowex 1	106
$[Rh\{(R)\text{-pn}\}Cl_4]^-$	$[Rh(pn)_2Cl_2]^+$, $[Rh(pn)_3]^{3+}$	column; Dowex 1	51a
Bis[1,3-(2′-pyridyl)-1,2-diaza-2-propenato]-rhodium(III) chloride	$RhCl_3$, ligand	column; Chromedia P-11 (cellulose phosphate)	6
Tris[1,3-(2′-pyridyl)-1,2-diaza-2-propenato]rhodium(III) chloride	corresponding ClO_4^-	column; Deacidite FF (anion exchange resin)	6

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[a] HAcac = acetylacetone; Acac = acetylacetonate ion; [b] en = ethylenediamine; Ham = amino acid; am = amino acid anion; [c] trien = triethylenetetramine; [d] gly = glycinate ion; val =valinate ion; [e] hfac = hexafluoroacetylacetone; fac = hexafluoroacetylacetonate ion; [f] Ox = $C_2O_4^{2-}$.

the reaction yields are small or where the desired compound is of high value such as in the preparation of complexes of the platinum metals.

The general choice of ion exchange column methods is again a logical one for most preparations and purifications. Whereas separation of product from reactants is usually quite easy, separation of product from by-products is often more difficult because of similarities in charge and structure. Yet, even with ion exchange resins, it is possible to separate geometric isomers[15,34,100,101].

Use of silica gel, alumina, or cellulose as column adsorbents has been most frequent in cases where the complexes to be separated are of very similar charge to the reactants or where neutral complexes are involved.

Table 3 summarizes some of the applications of chromatography to preparative coordination chemistry. The work of Connick and Fine[34] illustrates the specificity of ion exchange methods. By using both cation and anion resins, they were able to separate other isomers from a solution containing the desired product $[Ru(H_2O)_3Cl_3]$, and then were able, by chromatography, to identify the presence of two isomers of neutral trichloroaquoruthenium(III) complexes.

Another very useful preparative application of chromatography, on cellulose, is that of Buckingham and co-workers[18,19]. In studying the reaction between some cobalt(III) hydroxoaquotetramines and amino acids, they used cellulose chromatography (paper, thin-layer, and column) to separate the resulting amino acid cobalt complex from unreacted amino acid and other reaction products.

Thus far, preparative chromatography has been limited largely to octahedral complexes; only a few examples[26,27,142], involving square planar complexes appear in the literature. The technique is not limited to mononuclear complexes but has also been applied to polynuclear complexes[50a].

D. SEPARATION OF DIFFERENT COORDINATION COMPLEXES OF THE SAME ELEMENT

This type of chromatography of coordination complexes is very closely related to the previous type except that here will be included those separations that are used primarily to study reaction kinetics and to determine the charge on a coordination species.

The number of square planar complexes investigated is few compared to the number of octahedral complexes separated. Thus it is difficult at present to report whether the trends observed in the separation of octahedral complexes apply as well to complexes of other coordination numbers.

(i) Complexes with different charges

In several publications[23,59,100,101,116,144], chromatographic separation has been used to follow the rate of hydrolysis reactions. In these reactions, an anionic

TABLE 4

SEPARATION OF DIFFERENT COMPLEXES OF THE SAME ELEMENT BY CHROMATOGRAPHY

Complex	*Stationary phase*	*Purpose*	*Ref.*
Co^{III} amines	thin-layer; silica gel	identification	39
Co^{III} nitroammines	column; alumina	charge identification	61
Co^{III} nitroammines	paper	separation	82
Co^{III} nitroammines	ion electrophoresis	charge identification	102
Co^{III} nitroammines	paper	separation	157
Co^{III} amines	paper	charge identification	158
Ethylenediamine-*l*-propylenediamine complexes of Co^{III}	cellulose	identification	42
$[Co(NH_3)_4X_2]^+$	ion electrophoresis	follow kinetics	124
Co^{III} ammines	paper	separation	119
$[Co(en)_2X_2]^{n+}$[a] ($X = Cl$, Br, NCS, NO_2)	ion electrophoresis	separation	10
$[Co(en)_2Ac_2]^+$[b], $[Co(en)_2(H_3O)Ac]^{2+}$	column; Dowex 50	follow kinetics	23
$[Co(en)_2Ac_2]^+$, $[Co(en)_2(H_2O)Ac]^{2+}$	ion exchange paper; Amberlite SA-2	follow kinetics	24
Cr^{3+}, $[Cr(H_2O)_5(NCS)]^{2+}$, $[Cr(H_2O)_4(NCS)_2]^+$	column; Dowex 50	separation	76
$[Cr(H_2O)_4Ox]^+$, $[Cr(H_2O)_2Ox_2]^-$[c]	column; Dowex 50	follow kinetics	21
$[Cr(H_2O)_5X]^{2+}$ ($X = F$, Cl, Br, I)	column; Dowex 50	separation, follow kinetics	117
Cr^{III} ammines	column; Dowex 50	follow kinetics	123
$[Cr(en)NH_3(H_2O)\ Br_{3-x}]^{x+}$ ($x = 1, 2, 3$)	column; Dowex 50	identification	59
$[Cr(en)_2(OH)_2]^+$, $[Cr(en)_2Cl_2]^+$	column; Dowex 50	follow kinetics	116
$[Cr(en)_2Cl_2]^+$, $[Cr(en)_2(H_2O)Cl]^{2+}$	column; Dowex 50	follow kinetics	100
Cr^{III} amines	thin-layer; silica, alumina	separation; identification	80
$[Cr(en)_2Cl_2]^+$, $[Cr(en)_2(H_2O)Cl]^{2+}$, $[Cr(en)_2(H_2O)_2]^{3+}$	column; Dowex 50	follow kinetics	101
$[Cr(en)_2F_2]^+$, $[Cr(en)_2(H_2O)F]^{2+}$	column; Dowex 50	follow kinetics	49
$[Cr(trien)Ox]^+$[d]	column; Dowex 50	follow kinetics	143
$[Cr(en)_2Cl(NCS)]^+$, $[Cr(en)_2(H_2O)Cl]^{2+}$	column; Dowex 50	follow kinetics	144
$[Ir(Et_2S)_3Cl_3]$	ion electrophoresis	charge identification	72
$[IrCl_3(CO)\{(C_6H_5)_2PCH_3\}_2]$	thin layer; silica gel	identification	30
$[Mo(CO)_4\{(C_4H_9)_3P\}\text{-}\{(C_6H_5)_3PO\}]$	column; alumina	identification	51
Pt^{II} ammines	paper	identification	4
Pt^{II} amines	thin-layer; silica gel	identification	40
Rh chloro complexes	ion electrophoresis; paper; ion exchange	charge identification	96
Ru chloro complexes	column; Dowex 50	identification	22
Ru chloro complexes	column; Dowex 50, Dowex 1	identification	33
$[Ru(NO)(H_2O)_{5-x}(NO_3)_x]^{3-x}$	column; Dowex 50	identification	130

[a] en = ethylenediamine; [b] Ac = acetate ion; [c] Ox = $C_2O_4^{2-}$; [d] trien = triethylenetetramine.

ligand was replaced by water, resulting in an increase in the charge on the complex. One important limitation to the use of chromatography in the study of reaction kinetics is the fact that no further reaction should take place either with the eluent or between the resin or stationary phase and the adsorbed complex. This restricts the use of chromatography to inert complexes such as those of cobalt(III), chromium(III), and a few other elements, for which reaction times are long compared to the time required to chromatograph the substance.

One of the commonest types of reaction of coordination complexes that has been investigated is a solvolysis reaction in which a solvent molecule replaces one of the ligands, usually an anionic ligand so that the resulting reaction product has a higher charge than the initial complex.

Here again ion exchange is the most popular method as would be expected for separations based on differences in charge. However, inasmuch as many of the separations were developed for the purpose of identification and characterization of ionic charge on a micro or semimicro scale, there are numerous examples of paper chromatographic, thin-layer chromatographic, and ion electrophoretic methods. In most cases, acidic aqueous solvents have been used with a variety of stationary phases. Although separation of octahedral complexes, especially those of chromium(III) and cobalt(III), predominate, several examples of the separation of square planar coordination complexes have appeared in the literature.

It is interesting to compare the results in the first six references in Table 4 for the separation of the various nitroamminecobalt(III) ions, $[Co(NH_3)_{6-x}(NO_2)_x]^{(3-x)+}$. Although different techniques (column, thin-layer, and paper chromatography; and ion electrophoresis) were used in these experiments, in every case the ionic mobility could be related to the charge on the complex; the chromatographic ionic mobility decreased with increasing charge on the complex. In the case of ion electrophoresis, ionic mobility toward the electrode of opposite polarity from the charge was enhanced by the increased absolute charge on the ion.

In some cases, the chromatographic method was used specifically to characterize the charge on the complex. Kauffman *et al.*[72] and Maddock and Todesco[102] both used ion electrophoresis in their studies of complexes of type $[MX_3Y_3]$ to show that what were supposedly two geometric isomers of a neutral complex were instead the neutral complex and one "polymerization" isomer.

Yoneda's recent study[158] of the paper chromatography of some cobalt(III) amines, in which a 1M aqueous solution of ethylamine was used as developer, suggests that the R_F values can be correlated with the charge on the ion. Ions of 3+ charge have $R_F = 0.10–0.20$; 2+ ions, $R_F = 0.20–0.30$; 1+ ions, $R_F = 0.40–0.60$; neutral complexes, $R_F = 0.70–0.85$; 1 − ions, $R_F = 0.85–0.90$, and 3− ions, $R_F = 0.95–1.00$.

The work of Pollard, Banister, Geary and Nickless[119] is interesting for its inconsistency when compared to other similar separations of cobalt(III) amine complexes. They found little relation between R_F values and charge or geometry of the complexes—features that are present in all other research on the subject. They did report some secondary spots and considerable tailing in the chromatography of some of their complexes, a fact which suggests that the complexes were undergoing some kind of decomposition either in solution or during the development of the chromatogram.

(ii) Complexes with the same charge

By the use of aqueous ethanol acidified with hydrochloric acid, Basolo *et al.*[5] were able to separate on paper the *cis* isomers of $[Pt(NH_3)_2X_2]$ ($X = Cl, Br, I$) from each otherand from the *trans* isomers, but not the *trans* isomers from each other. They accomplished the latter separations by use of acetone–water mixtures.

Dwyer and Sargeson[42] employed partition chromatography on cellulose to study the composition of the reaction product obtained from *l*-propylenediamine, and *cis*-dichloro- and *cis*-dinitrobis(ethylenediamine)cobalt(III) chlorides. The separations were repeated with a cellulose pulp column, and the complexes obtained in order of elution were L-$[Co(l\text{-}pn)_3]Cl_3$, L-$[Co(l\text{-}pn)_2\,en]Cl_3$, L-$[Co(en)_2\,l\text{-}pn]Cl_3$, D-$[Co(l\text{-}pn)_3]Cl_3$, D-$[Co(l\text{-}pn)_2\,en]Cl_3$, D-$[Co(en)_2\,l\text{-}pn]Cl_3$, and D,L-$[Co(en)_3]Cl_3$.

E. SEPARATION AND IDENTIFICATION OF GEOMETRIC ISOMERS

Most published separations of coordination complexes by chromatography involve the separation of geometric isomers of both octahedral and square planar complexes. These separations have been developed both for the preparation of isomerically pure complexes and for the identification of reaction products. In some cases[69,71], separations have been carried out quantitatively.

Whereas a number of separations of geometric isomers have been carried out on ion exchange resins, silica gel and alumina seem to offer sharper separations, especially for complexes of low ionic charge. The latter two substrates are also popular in thin-layer chromatography.

Certain limitations to the use of chromatography for the determination of geometric configuration must be noted. As Burwell *et al.*[20] have pointed out, prolonged contact of some complexes with silica gel results in substitution of the silica gel for a ligand. For cobalt(III) complexes, this substitution would undoubtedly be enhanced by use of a basic solvent. For other complexes, prolonged contact with a solvent might result in solvolysis reactions which yield a change in configuration. The thin-layer chromatographic separation of some cobalt(III) amines on silica gel by Seiler, Biebricher and Erlenmeyer[133] seems to provide evidence both for hydrolysis and for geometric rearrangement of some of the complexes.

Although they supposedly used pure complexes for their chromatograms, on development more than one spot appeared.

Isomerization on a silica gel column was observed with $[Pt\{(C_4H_9)_3P\}_2Cl_2]$ by Kauffman *et al.*[71]. The melting points showed that the recovered isomers were pure; the ratio of *cis* isomer to *trans* isomer had changed significantly although the *total* weight of *both* recovered isomers indicated that the separation was quantitative.

Overwhelming evidence exists that for octahedral complexes developed with an acidic or water-containing solvent, the *trans* isomer is more mobile than the *cis* isomer. This regularity has been used, along with other evidence, to assign to $[Cr(en)_2(H_2O)F]^{2+}$ a *trans* configuration[142a]. Burwell *et al.*[20] suggest that the *cis* isomer can have two points of attachment to the silanol sites of the silica gel or, by analogous reasoning, to the acidic sites of an ion exchange resin, whereas the *trans* groups, being on opposite sides of the complex, can attach at only one point. Even if the mechanism is one of mere adsorption rather than ion exchange, this trend should still prevail since the *cis* isomer would be more polarized than the *trans* isomer. As an interesting case in point we may cite Kyuno's separations[90,91] of $[Co(NH_3)_2(CO_3)(NO_2)_2]^-$ and $[Co(NH_3)_2(C_2O_4)(NO_2)_2]^-$ on an alumina column. In both cases, the order of elution of the three possible geometric isomers was *trans*-NO_2 > *trans*-NH_3 > *cis* isomer. In terms of charge polarization, the least polarized ion is thus the most mobile.

As a perusal of Table 5 will show, in a few cases involving square planar complexes[5,64], exceptions are found to this general rule that the *trans* isomer is more mobile than the *cis* isomer. Exceptions to the *trans* > *cis* mobility rule are also found for octahedral complexes[65,115,130,140,141,157]. In the two papers on the paper chromatography of cobalt(III) amine complexes by Stefanović and Janjić[140,141] and the one by Yamamoto, Nakahara, and Tsuchida[157], the *cis* isomer always exhibits a higher R_F value than the corresponding *trans* isomer. Unfortunately, Yoneda[158] did not attempt to separate geometric isomers by paper chromatography. He reported only the R_F values for *cis*- and *trans*-$[Co(en)_2(NO_2)_2]NO_3$, which were identical. In another study of the effect of ionic charge on mobility, Pollard *et al.*[119] provide data only for *cis*- and *trans*-$[Co(NH_3)_4(NO_2)_2]^+$ where $R_F(trans) > R_F(cis)$. Despite Yoneda's claim that even paper has ion exchange properties, solvent properties may also play an important role in paper chromatography of charged complexes.

A problem that has not yet been fully solved is the separation of geometric isomers of 2+ or 3+ charge. Unfortunately, separations on paper or thin-layer adsorbents are not as sensitive for the more highly charged ions as they are for the 1+, or 1−, or neutral complexes. Yet in the study of solvolysis reactions, it is the rapid determination of the geometric configuration of the solvolysis products that is often crucial to the interpretation of the reaction mechanism.

It may be in order to mention here separations of complexes which are iso-

TABLE 5

SEPARATION OF GEOMETRIC ISOMERS OF COORDINATION COMPLEXES BY CHROMATOGRAPHY

Complex	*Stationary phase*	*Relative mobility*	*Ref.*
Trisbenzoylacetonates of Co, Cr, and Rh	column; alumina	*trans* > *cis*	47
Tristrifluoroacetylacetonates of Co, Cr, and Rh	column; alumina	*trans* > *cis*	48
Co^{III} amines	paper	*trans* > *cis*	82
Co^{III} amines	paper	irregular	119
Co^{III}amines	paper	*cis* > *trans*	140
Co^{III} amines	paper	*cis* > *trans*	141
Co^{III} amines	paper	no difference	158
$[Co(NH_3)_4(NO_2)_2]^+$	paper	*cis* > *trans*	157
$[Co(NH_3)_4Cl_2]^+$, $[Co(NH_3)_4(H_2O)Cl]^{2+}$, $[Co(NH_3)_4(NO_2)_2]^+$	ion electrophoresis	—	124
Co^{III} amines	thin-layer; silica gel	*trans* > *cis*	39
$[Co(NH_3)_4(N_3)_2]^+$	column; alumina	*trans* > *cis*	99
trans(RS meso)-$[CoL(H_2O)Cl]^{2+}$ (L = 1,4,8,11-tetra-azaundecane)	column; Dowex 50	—	52
$[Co(NH_3)_3(NO_2)_3]$	ion electrophoresis	*trans* > *cis*.	102
$[Co(NH_3)_4(NO_2)_2]^+$	column; Dowex 50	*trans* > *cis*	77
$[Co(NH_3)_4(NO_2)_2]^+$, $[Co(en)_2(NO_2)_2]^{+a}$	column; Amberlite IR120	*trans* > *cis*	110
$[Co(en)_2(NO_2)_2]^+$	paper	*cis* > *trans*	65
$[Co(en)_2X_2]^+$	column;Amberlite IR 120	*trans* > *cis*	111
$[Co(en)_2X_2]^+$	ion electrophoresis	*trans* > *cis*	10
$[Co(en)_2Cl_2]^+$	column; Dowex 50	*trans* > *cis*	37
$[Co(en)_2XY]^+$	thin-layer; silica gel	*trans* > *cis*	133
$[Co(pn)_2(NO_2)_2]^+$	paper	*cis* > *trans*	65
$[Co(en)EDDA]^+$, $[Co(NH_3)_2EDDA]^{+b}$	column; Dowex 50	*trans* > *cis*	97
$[Co(en)(gly)_2]^{+c}$	column; Dowex 50	*trans* > *cis*	106
$[Co(gly)_2Ox]^{-d}$	column; Dowex 1	*trans* > *cis*	106
$[Co(en)_2(Ac)_2]^{+c}$	ion exchange paper; Amberlite SA-2	*trans* > *cis*	24
Bis(2,3-diaminopropionato)-cobalt(III) chloride	column; Dowex 50	—	50b
$[Co(en)_2(H_2O)_2]^{3+}$	column; alumina	*trans* > *cis*	61
$[Co(en)Ox(NO_2)_2]^-$	column; Dowex 1	*trans*-NO_2 > *cis*	88
$[Co(en)Ox(NO_2)NCS]^-$	column; Dowex 1	*trans* > *cis*	89
$[Co(NH_3)_2CO_3(NO_2)_2]^-$	column; Dowex 1	*trans*-NO_2 > *trans*-NH_3 > *cis*	90
$[Co(NH_3)_2Ox(NO_2)_2]^-$	column; Dowex 1	*trans*-NO_2 > *trans*-NH_3 > *cis*	91
$[Co(alin)_3]^f$	column; alumina; thin-layer; silica gel	*trans* > *cis*	25
$[Cr(H_2O)_4Cl_2]^+$	column; Dowex 50	*trans* > *cis*	78
Tris(acetylacetanilido)-chromium(III)	column; alumina	*trans* > *cis*	135
Tris(acetylacetanilido)-chromium(III)	thin-layer; silica gel	*trans* > *cis*	134

TABLE 5 *(continued)*

Complex	*Stationary phase*	*Relative mobility*	*Ref.*
Cr^{III} amines	column; alumina	*trans* > *cis*	9
[Cr(en)(NH$_3$)(H$_2$O)$_2$Cl]$^+$	column; Dowex 50	I > II	59
[Cr(en)$_2$Cl$_2$]$^+$, [Cr(en)$_2$(H$_2$O)Cl]$^{2+}$	column; Dowex 50	*trans* > *cis*	100
[Cr(en)$_2$(H$_2$O)Cl]$^{2+}$	column; Dowex 50	*trans* > *cis*	101
[Cr(en)$_2$(H$_2$O)NCS]$^{2+}$	column; Dowex 50	*trans* > *cis*	144
[Cr(en)$_2$(OH)$_2$]$^+$	column; alumina	*trans* > *cis*	155
[Cr(H$_2$O)$_4$(NCS)$_2$]$^+$	column; Dowex 50	*trans* > *cis*	55
[Cr(H$_2$O)$_4$Cl$_2$]$^+$	column; Dowex 50	*trans* > *cis*	78
Iron carbonyls	column; alumina	—	14
[CH$_3$SFe(CO)$_3$]$_2$	column; alumina	*anti* > *syn*	28, 79, 80
cis-[Ir{(C$_2$H$_5$)$_2$S}$_3$Cl$_3$]	electrophoresis	electrolyte > nonelectrolyte	72
[Cu(gly)$_2$][c]	paper	*cis* > *trans*	64
[Mn(CO)$_3${(C$_6$H$_5$)$_3$P}$_2$SCN]	column; alumina	—	155
Pt^{II} ammines	paper	*cis* > *trans*	4, 5
Pt^{II} amines	thin-layer; silica gel	*trans* > *cis*	40
Pt^{II} amines (mononuclear and binuclear)	thin-layer; silica gel	*trans* > *cis*	69
Pt^{II} amines (mononuclear and binuclear)	column; alumina	*trans* > *cis*	71
[Rh(H$_2$O)$_2$Cl$_4$]$^-$	column; Dowex 1	*trans* > *cis*	15, 50
[Ru(H$_2$O)$_3$Cl$_3$]	column; Dowex 50	*trans* > *cis*	32, 34, 50
[Ru(H$_2$O)$_4$Cl$_2$]$^+$	column; Dowex 50	*trans* > *cis*	33, 50
[Ru(H$_2$O)$_3$Cl$_3$]	column; Dowex 50, 1	*trans* > *cis*	50, 107
[Ru(NO)(H$_2$O)$_{5-x}$(NO$_3$)x] $^{3-x}$+ (x < 5)	paper	—	130
[Ru(NO) (H$_2$O)$_{5-x}$(NO$_3$)$_x$] $^{3-x}$+ (x > 5)	Zeo-Karb 225 cation exchange resin	*cis* > *trans*	130
[PtL$_2$Cl$_4$] (L = (C$_2$H$_5$)$_2$S, (C$_4$H$_9$)$_3$P)	column; alumina, silica gel	*trans* > *cis*	68
Alkyl and aryl derivatives of Pt^{II} phosphines	column; alumina	*trans* > *cis*	26, 27
[CH$_3$COMn(CO)$_4$–P(C$_6$H$_5$)$_3$]	thin-layer and column; silica gel	*cis* > *trans*	115
[Pt(NH$_3$)$_2$X$_2$] (X = Cl, Br, I)	paper	—	5
Ditolyltellurium(II)	thin-layer; alumina	*ortho* > *meta* > *para*	148
[Pt{(C$_4$H$_9$)$_2$S}Cl$_2$]	thin-layer; silica gel	*trans* > *cis*	68
[(C$_2$H$_5$)$_3$PAuSC(S)OR] (R = n or iso-propyl)	thin-layer; silica gel	*n* > *iso*	68
Cu(3,4- or 3,5-lutidine)$_x$–Cl$_2$(x = 2 or 4)	thin-layer; silica gel	3,5 > 3,4	68
[Pd(Et$_4$dien)SeCN]$^+$[g], [Pd(Et$_4$dien)NCSe]$^+$	thin-layer; silica gel	Se-bonded > N-bonded	68

[a] en = ethylenediamine; [b] H$_2$EDDA = ethylenediamine-*N,N'*-diacetic acid; EDDA = its binegative anion; [c] gly = glycinate ion; [d] Ox = C$_2$O$_4^{2-}$; [e] Ac = acetate ion; [f] alin = β-alaninate ion; [g] Et$_4$dien = *N,N,N',N'*-tetraethyldiethylenetetramine.

meric by virtue of isomerism within the ligand itself, such as the TLC separations of di-*o*-, *m*-, and *p*-tolyltellurium(II) by Vobecky[148] and of dichlorobis(n-, iso-, sec-, and t-butyl sulfide)platinum(II) (geometric isomers also), bis- or tetrakis-(3,4- or

3,5-lutidine)copper(II) chlorides, and *0*-n- or iso-propyldithiocarbonato(triethylphosphine)gold(I) by Kauffman[68]. Work on the TLC separation of linkage isomers is currently in progress in Kauffman's laboratory. The separation of Se-bonded from N-bonded [Pd(Et_4dien)SeCN] [$B(C_6H_5)_4$] has already been achieved[68].

F. RESOLUTION OF OPTICALLY ACTIVE COORDINATION COMPLEXES

A rapid, efficient, and general method for separating optical isomers of coordination complexes has long been a goal sought by inorganic chemists. Indeed, Alfred Werner, the founder of coordination chemistry, used resolution to establish unequivocally the octahedral configuration for tripositive cobalt[66,67]. Often today, a structure-proof depends upon proving the existence of optical isomers. Pasteur's

TABLE 6

RESOLUTION OF OPTICAL ISOMERS OF COORDINATION COMPLEXES BY CHROMATOGRAPHY

Complex	*Stationary phase*	*Purpose*	*Ref.*
$[M(Acac)_3]^a$ (M = Co, Cr)	alumina and D-tartaric acid; D-quartz	partial resolution	118
$[Co(Acac)_3]$	column and thin-layer; D-quartz	partial resolution	46
Tris(hexafluoroacetylacetonato)chromium(III)	D-quartz (gas chromatography)	partial resolution	139
Hexakis(2-aminoethanethiolo)tricobalt(III) cation	Ion exchange cellulose	total resolution	16
$[Co(en)_3]^{3+}$, $[Co(gly)_3]^b$	starch	partial resolution	84
Co L-methylxanthate	alumina	total resolution	85
trans-$[Co(gly)EDDA]^c$	starch	partial resolution	98
1,2,6-$[Co(alin)_3]^d$	L-quartz	partial resolution	25
$[Co(en)_2X_2]^+$	paper	partial resolution	140
$[Co(Acac)_3]$, $[Rh(Acac)_3]$	D-lactose	partial resolution	29
$[Co(Acac)_3]$, $[Cr(Acac)_3]$	D-lactose	partial resolution	108
Cu, Ni β-ketoimines	D-lactose	partial resolution	58
Vanadyl ketoimine and diketoimine	D-lactose	partial resolution	126
Bisacetylacetonepropylenediiminooxovanadium(IV)	D-lactose	partial resolution	104, 125
$[Y(Acac)_3]$, $[Ga(Acac)_3]$	D-lactose	partial resolution	109
Diphenylbis(acetylacetonepropylenediimino)tin(IV)	D-lactose	partial resolution	127
Bis(N-R salicylaldimino)MII (M = Zn, Cu, Ni, Co; R = C_6H_5, isopropyl, cyclohexyl)	D-quartz	partial resolution	46
$[NiL]I_2(L{=}N({-}CH_2{-}CH_2{-}{-}N{=}CH{-}C_5H_4N)_3)$	cellulose	partial resolution	154

[a] Acac = acetylacetonate ion; [b] gly = glycinate ion; [c] EDDA = ethylenediamine-*N,N′*-diacetate dinegative anion; [d] alaninate ion.

classical fractional crystallization of diastereoisomers, which is still the most widely used method of resolution, is tedious, inefficient, and not always reliable. In a recent article on future developments in analytical chemistry. L. B. Rogers[129] predicts that a rapid quantitative *chromatographic* separation of optical isomers will be a major advance within the next five years.

A few separations, on a small scale basis, have been reported, but most of these have yielded only partial resolution of the enantiomers. All of the methods are based on the presence of an optically active resolving agent in the stationary phase. With neutral complexes, such as acetylacetonates and β-ketoimines[29,58,104,108,109,125,126], that are soluble in organic solvents, D-lactose has been used quite successfully. The chromatographic resolution of a pentacoordinate complex is of more than passing interest[125,126]. In separations where aqueous solvents were used, D-quartz seemed to give the best results.

A very tantalizing sentence appeared in Stefanović and Janjić's note[140] on the paper chromatography of some ethylenediamine complexes of cobalt(III) in which they claimed to have separated, on paper, the optical antipodes of *cis*-$[Co(en)_2Cl_2]^+$. However, in their subsequent paper[141], which gives a more detailed account of their experimental procedures, no mention is made of the separation of optical isomers. Perhaps their first reports may have been based on impurities in their developed chromatograms.

While all separations to date (See Table 6) utilize a resolving agent in the stationary phase, a recent novel paper by Bosnich[13] suggests that better results might be achieved by use of an optically active solvent. By use of L-2,3-butanediol, he observed that a solution of *cis*-$[Co(en)_2Cl_2]^+$ slowly antiracemized to its active isomer. It is quite possible that such a solvent used in chromatography would preferentially desorb one enantiomer from silica gel, alumina, or cellulose, thereby achieving a rapid resolution.

G. SUMMARY

Recent applications of the various types of chromatography (column, thin-layer, paper, ion exchange, and electrophoresis) to the separation, preparation, identification, purification, and resolution of coordination complexes have been briefly reviewed. The techniques have also been used to study reaction kinetics and to determine the charges of such complexes. Despite the rapid progress in the last two decades, a few problems remain to be solved, such as the separation of geometric isomers of high ionic charge and more efficient resolution of optical isomers.

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