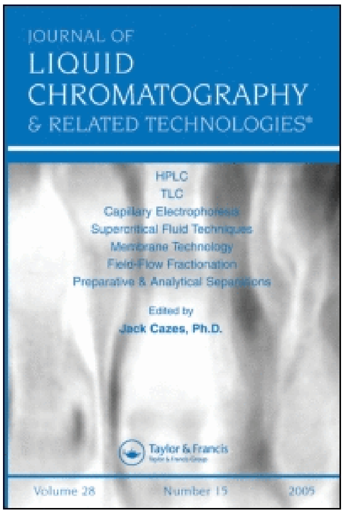


Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

Chromatographic Separation of Some Inorganic Isomers

R. K. Upadhyay[a]; Vasundhra K. Sharma[a]; V. P. Singh[a]
[a] Department of Chemistry, N.R.E.C. College, KHURJA, INDIA

To cite this Article Upadhyay, R. K. , Sharma, Vasundhra K. and Singh, V. P.(1982) 'Chromatographic Separation of Some Inorganic Isomers', Journal of Liquid Chromatography & Related Technologies, 5: 6, 1141 — 1153
To link to this Article: DOI: 10.1080/01483918208067574
URL: http://dx.doi.org/10.1080/01483918208067574

JOURNAL OF LIQUID CHROMATOGRAPHY, 5(6), 1141-1153 (1982)

CHROMATOGRAPHIC SEPARATION OF SOME INORGANIC ISOMERS

R.K. Upadhyay*, (Miss) Vasundhra K. Sharma and V.P. Singh
Department of Chemistry, N.R.E.C. College, KHURJA - 203131, INDIA

ABSTRACT

Isomeric simple complexes of Ti(III) and Hg(II) with p-diethylaminoanil of anthraceneglyoxal (DEAAnG) and isomeric mixed ligand complexes of Zn(II) with DEAAnG and Thiourea (TU) have been synthesized, resolved in bulk on silica gel column, and characterized on the basis of elemental analyses, molar conductance and infrared studies.

Binary mixtures of isomers have been analysed by TLC, PC and EC techniques. TLC method showing highest resolving capacity was used in the quantitative analysis of isomeric mixtures. Resolved isomers were identified using i.r. and migration rate correlations.

INTRODUCTION

While testing the homogeneity of simple complexes of Ti(III) and Hg(II) with DEAAnG and mixed ligand complexes of Zn(II) with DEAAnG and thiourea, they were found to be binary mixtures.

---

* Address for correspondence - 837, Sarai Nasrulla
(Behind Thana Dehat)
KHURJA - 203131,
INDIA

Binary mixtures were resolved in bulk on silica-gel column and characterized on the basis of chemical analyses, molar conductance and infrared studies.

Although, a number of attempts have been made for the separation and identification of inorganic isomers by chromatographic techniques[1-3] like TLC and PC, yet they are quite a few as compared with those on organic isomers. This fact aroused our interest to undertake analytical studies on the Ti(III), Hg(II) and Zn(II) isomeric complexes using chromatographic methods. In the present communication separation, identification and determination of a few new inorganic isomers by TLC, PC and EC have been reported. TLC method was found to be superior to PC and EC in its separation efficiency.

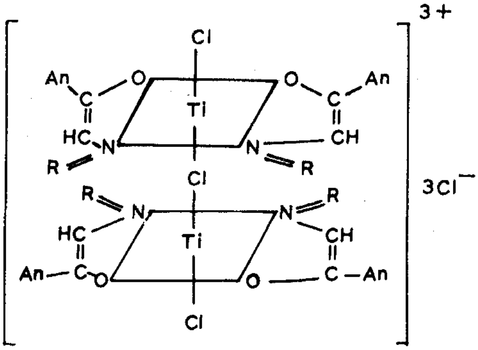
EXPERIMENTAL

Isolation of DEAAnG and its Complexes

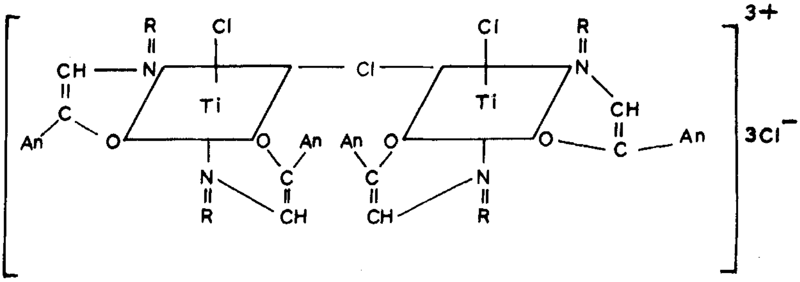
p-Diethylaminoanil of anthraceneglyoxal was precipitated from the equimolar mixture solution of anthraceneglyoxal and p-aminodiethylaniline in ether at room temperature. Compound was purified by recrystallization from acetone.

Complexes of DEAAnG with Ti(III), Hg(II) and Zn(II) ions were prepared by mixing the reactant solutions in acetone or alcohol in stoichiometric ratios. Solids were isolated either by evaporating the reaction mixture or by increasing its pH with NaOH solution (in case of Ti(III) complex). Products were finally washed with ether till excess ligand was washed out. Mixed ligand complex of Zn(II) was prepared by mixing Zn(II)-DEAAnG complex and thiourea in 1:1 ratio in acetone solvent. Reaction

Ti(III)-DEAAnG (a) (Cis)



Ti(III)-DEAAnG (b) (Trans)



mixture was evaporated on water bath and solid was washed with water and ether till excess reactants were removed. Complex was dried in oven at 80°C.

Chemicals used in the synthetic work were B.D.H. or S.M. Laboratory reagents.

Analysis and Physical Measurements

Infrared spectra of the compounds were recorded in CsI medium on Perkin Elmer grating infrared spectrophotometer model - 577 in the range 200 - 4000 cm^{-1}. Conductometric measurements were made with Toshniwal conductivity bridge using dip-type cell. Elemental analysis was performed by routine micro analytical methods at C.D.R.I., Lucknow (INDIA).

Preparation of Column for Separation of Isomers

Chromatographic column tube of 50 cm length and 2 cm diameter provided with a stop cock at the lower end was mounted vertically and gel layer was prepared by pouring suspension of silica gel (50 -100 mesh BDH) in acetone as usual. Acetonic solution of each binary isomeric mixture was poured into the column and allowed to run. Fast moving isomer was collected in beaker and slow moving one with low R_F which retained in the column was eluted by EtOH. Solutions were evaporated to dryness and complexes were recrystallized from acetone.

Preparation, Loading and Development of TLC Plates and PC and EC Paper Strips

Silica gel G (BDH) mixed with starch binder (19:1, w/w) was used to prepare 0.1 cm layers on 3x10 cm glass plates. A home-built apparatus[4] was used to spread aqueous slurry on the plates. Sample solutions prepared in EtOH or Me_2CO were applied with fine capillaries on dry plates and development was done in rectangular glass chambers with ground-in-lids by the ascending technique. The solvent front was allowed to migrate for a fixed distance of 6-8 cms and development time was noted. For quantitative work 10x15 cm plates were loaded with known volumes of standard sample solutions by micro-pipettes. Chromatogram fragments were scraped and eluted with EtOH/Me_2CO. Optical densities of the elutes were determined at the λmax of their elutes and concentrations of the complexes were then deduced from their respective calibration curves prepared under similar conditions of solvent and temperature.

In paper chromatography Whatmann No.1 3x15 cm filter paper strips were loaded with fine capillaries in 2-3 mm spots and developed in cyclindrical glass jars, already saturated with solvent. Time of development was noted for 6-8 cms distance travelled by the solvent front.

Electrochromatography was carried out in vertical type apparatus, Whatman No.1 paper strips (3x35 cm) were loaded at the centre by fine capillaries. Loaded strips were hanged with both ends in the electrode solvents and apparatus was closed. At saturation stage constant voltage was applied and after 2 - 3.5 hours chromatograms were taken out and dried.

No locating agent was needed as spots were visible in day light.

RESULTS AND DISCUSSION

Stoichiometric Studies

Homogeneinity test of complex by TLC using acetone as developing solvent revealed that Ti(III)-DEAAnG, Hg(II)-DEAAnG and Zn(II)-DEAAnG-TU are the binary isomeric mixtures which could be separated in bulk by column chromatography using acetone solvent. Stoichiometry of the isomeric complexes was deduced from analytical data (Table - 1). Molar conductance values[5,6] and silver nitrate test revealed that all compounds are ionic.

A comparison of infrared spectra of ligands with their corresponding complexes revealed negative shift in the frequencies of C=O, C=N groups of DEAAnG, C=S group of thiourea clearly indi-

TABLE - 1

λmax, Λ_M (Ω^{-1} mole^{-1} cm^{2}), Elemental Data and Important I.R. Frequencies

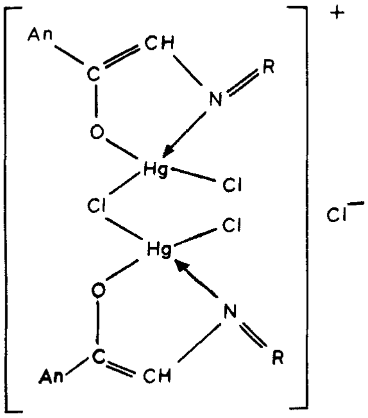
Complex	λmax (visible)	Λ_M	Elemental Analysis Calcd./Found(%)			Infrared Frequencies (cm^{-1})							
			C	H	N	C=O	C=N	C=S	M-N	M-O	M-Cl	M-Cl-M	M-S
$[Ti_2(DEAAnG)_4Cl_3].Cl_3$(a) (cis)	420	440.64 (EtOH)	68.24 (68.92)	5.24 (5.04)	6.12 (6.38)	1740	1650	-	470	400 210	295	240	-
$[Ti_2(DEAAnG)_4Cl_3].Cl_3$(b) (trans.)	610	725.11 (Me_2CO)	68.24 (67.88)	5.24 (5.38)	6.12 (6.24)	1740	1680	-	470	320 220	-	270	-
$[Hg_2(DEAAnG)_2Cl_3].Cl$ (a) (tetra.)	420	195.48 (MeCN)	47.88 (48.02)	3.68 (3.49)	4.29 (4.40)	1730	1610	-	470	220	285	-	--
$[Hg_2(DEAAnG)_2Cl]$ $.Cl_3$(b) (trigo.)	600	749.34 (Me_2CO)	47.88 (48.15)	3.68 (3.80)	4.29 (4.19)	1740	1660	-	520	460	-	265	-
$[Zn_2(DEAAnG)_2(TU)_2Cl].Cl_3$ (a) (Sq. planar)	480	357.72 (EtOH)	54.70 (54.62)	4.72 (4.84)	9.45 (9.19)	1680	1620	1055	540	480	-	265	-
$[Zn_2(DEAAnG)_2(TU)_2Cl].Cl_3$ (b) (tetra.)	580	451.67 (Me_2CO)	54.70 (54.90)	4.72 (4.59)	9.45 (9.65)	1650	1620	1065	510	310	-	290	275

cating their participation in coordination. Some new bands which could be assigned to M-O, M-N, M-Cl and M-S bonds, appeared in the spectra of complexes (isomers) confirm the coordination through C=O, C=N and C=S groups of the ligands.

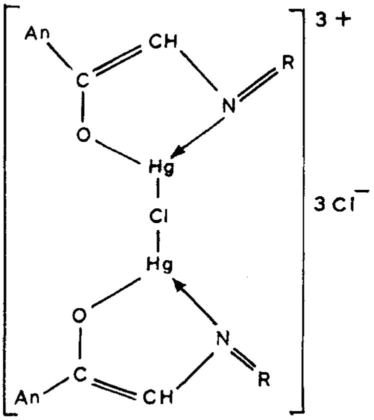
Octahedral complexes of the type $M(AA)_2X_2$ (AA = bidentate ligand and X = halogen) are capable of exhibiting cis- and trans-isomerism. For cis isomers (C_{2v} symmetry) having axial positions of halogens one would expect two i.r. active M-X stretching modes while for trans isomer (D_{4h} symmetry) only one normal mode is expected. Based on these considerations cis- configuration may be proposed for binuclear Ti(III)-DEAAnG(a) complex and trans for binuclear Ti(III)-DEAAnG(b) complex.

In Hg(II) - DEAAnG(a) complex showing 1:1 electrolytic nature infrared band at 285 cm^{-1} which could be assigned to Hg-Cl stretching indicated free chlorine coordinated with the metal ion. Although, Hg-Cl-Hg stretching frequency could not be identified, yet in the light of molar conductance and analytical

Hg(II)-DEAAnG (a) (Tetrahedral)

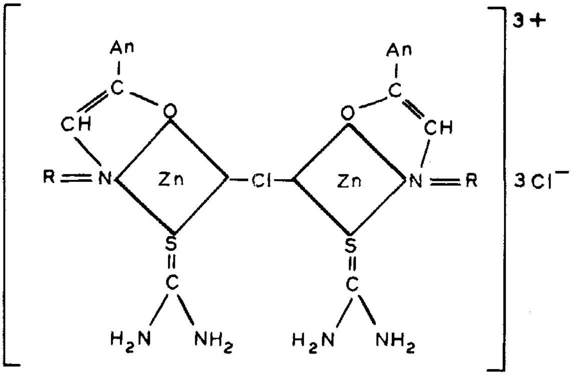


Hg(II)-DEAAnG (b) (Trigonal)

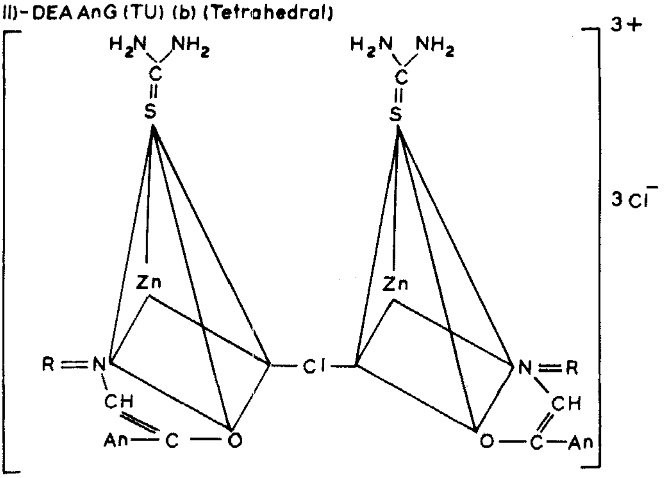


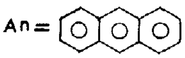
data possibility of halogen bridged binuclear structure cannot be ruled out. In Hg(II)-DEAAnG(b) complex appearance of only one i.r. band at 265 cm^{-1} corresponding to Hg-Cl-Hg stretching, molar conductance and analytical data indicated halogen bridged binuclear structure involving Hg(II) in three coordination number.

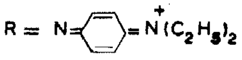
Zn(II)-DEAAnG (TU) (a) (Square Planar)



Zn(II)-DEA AnG (TU) (b) (Tetrahedral)







On the basis of chemical analysis and molar conductance data halogen bridged binuclear structure could be suggested to both Zn(II) complexes. Higher frequency of Zn-Cl-Zn stretching in Zn(II)-DEAAnG-(TU) (b) than in Zn-DEAAnG-(TU) (a) indicated tetrahedral stereochemistry of former and square-planar geometry of the later.

Based on the above studies the following structures may be proposed to the complexes:

Chromatographic Studies

Chromatographic data obtained by migrating individual complexes revealed the separation of all the binary mixtures of isomers by TLC, PC and EC. Although, complexes showed different migration rates in several solvents, only the solvents which could give best resolution of the mixtures have been noted in Table -2. Migration rates have been found to be independent on the plate and paper size, however, adsorbent layer thickness has adverse effect on it.

The stretching frequency (ν) values (Table - 1) of azomethine group of DEAAnG which is highly metal sensitive and λ max values have been correlated with migration rates of the complexes in resolving solvents. The new spectroscopic and chromatographic correlations useful in making certain identification of resolved components form an interesting feature of the present study.

Although, all the binary mixtures of complexes could be resolved and identified by all the three chromatographic methods, the quantitative separation, however, could only be achieved by TLC. The choice of TLC over PC and EC also lies in its quick resolution and high effectiveness of the solvent in it.

TABLE - 2

BEST RESOLVING SOLVENTS FOR DIFFERENT MIXTURES

Complexed Ligand(s)	Ions in mixtures	Resolving solvent	Chromatographic method of separation
DEAAnG	Ti(III) cis + Ti(III) trans (0.05) (1.00)	n-BuOH-C_6H_6 (1:1, v/v)	TLC
	Hg(II) tetrahedral + Hg(II) trigonal planar (0.07) (1.00)	n-BuOH	TLC
DEAAnG and TU	Zn(II) Square planar + Zn(II) tetrahedral (0.12) (0.92)	AcOH	TLC
DEAAnG	Ti(III) cis + Ti(III) trans (0.00) (0.93)	MeCN	PC
	Hg(II) tetra + Hg(II) trigo. (0.06) (0.95)		
DEAAnG and TU	Zn(II) Sq. planar + Zn(II) tetrahedral (0.08) (0.62)	Iso-BuCOMe	PC
DEAAnG	Ti(III) cis + Ti(III) trans (0.05) (1.5)	AcOH	EC
	Hg(II) tetra + Hg(II) trigo. (0.00) (3.1)	AcOH- $\frac{N}{10}$HCl (7:1, v/v)	EC
DEAAnG and TU	Zn(II) Sq. planar + Zn(II) tetra (2.5) (4.2)	AcOH - $\frac{N}{10}$HCl (7:3, v/v)	EC

Values given in parenthesis are the R_f values in TLC and PC and distance travelled by ions in cm in EC.

TABLE - 3

Maximum Quantities of Complexes Resolved by TLC

Mixture resolved	Spot colour	Weight of complex applied on plate (μg)	Weight of complex recovered (μg)	Error (%)
$[Ti_2(DEAAnG)Cl_3].Cl_3$ cis	Brown	2.55	2.55	0.00
$[Ti_2(DEAAnG)Cl_3].Cl_3$ trans	Gray	10.95	11.00	+0.45
$[Hg_2(DEAAnG)_2Cl_3]$ Cl (tetra.)	Pink	6.65	6.66	+0.15
$[Hg_2(DEAAnG)_2Cl]$ Cl_3(trigo.)	Green	4.75	4.73	-0.42
$[Zn_2(DEAAnG)_2(TU)_2Cl]Cl_3$ (Sq. planar)	Brown	6.25	6.22	-0.48
$[Zn_2(DEAAnG)_2(TU)_2Cl]$ Cl_3 (tetra.)	Pinkish-Gray	1.90	1.89	-0.52

Quantitative Separation

For quantitative analyses solutions of binary mixtures containing different quantities of isomeric complexes were applied on the TLC plates and developed in their resolving solvents. Chromatogram fragments scraped from the plate were eluted with acetone and optical densities of mixture components were measured at their λ max. Concentrations of elutes were deduced from standard calibration curves (O.D. v/s conc.) obtained under similar conditions of medium and temperature. Errors and limits of maximum separation (Table - 3) have also been found out in all the three mixtures. Isomeric compositions, that is, proportions of isomers (formed) were determined as 10:43, 14:10 and 33:10 in a and b isomers of Ti(III), Hg(II) and Zn(II) complexes, respectively. Several solvents showing wide difference in migration rates of the complexes indicated good possibility of their separation but owing to large diffusion and trailing effects they could not be used.

ACKNOWLEDGEMENT

We are thankful to N.R.E.C. College, Khurja for the experimental facilities, and to C.S.I.R. New Delhi for the award of J.R.F. to (Miss) Vasundhra K. Sharma.

REFERENCES

1. Y. Tsunoda, T. Takeuchi and Y. Yoshino, Sci. Papers Call. Gen. Educ. Univ. Tokyo, 14, 55 (1964).
2. G.B. Kauffman and B.W. Benson, Inorg. Chem., 6, 411 (1967).

3. G.B. Kauffman et.al., J. Chromatogr., 117, 455 (1976).

4. E. Stahl, Thin Layer Chromatography, Springer, Berlin ,2nd ed., P. 56, 1966.

5. B.P. Kennedy and A.B.P. Lever, Canad. J. Chem., 3488, 50 (1972).

6. S.M.F. Rehman, J. Ahmed and M.M. Haq. J. Inorg. Nucl. Chem., 35, 3351 (1973).