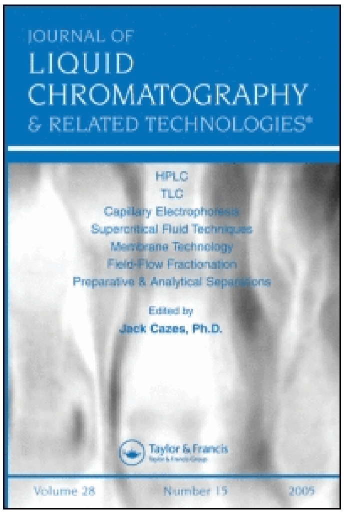

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CHROMATOGRAPHIC ANALYSIS OF SOME 3d METAL COMPLEXES

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ABSTRACT

Several quaternary mixtures of 3d transition metal ions (Ti(IV), Mn(II), Fe(III), Co(II), Cu(II) and Zn(II) complexed with p-diethylaminoanil of anthraceneglyoxal (DEAAnG) alone and alongwith thiourea (TU) have been resolved by TLC, PC and EC and identified using migration rate and spectroscopic (i.r.) correlations. The TLC method showing the best resolution has been used to separate quaternary mixtures of complexes quantitatively; coloured compounds have been estimated spectrophotometrically.

INTRODUCTION

Diverse chromatographic methods have been employed in the microanalysis of 3d metal ions as such and as their simple complexes with organic ligands and a few references[1-8] on chromatography of mixed ligand complexes are also available.

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However, no chromatographic studies have yet been made on simple complexes of ketoanils obtained from anthraceneglyoxal and mixed ligand complexes, involving ketoanils and thiourea as ligands. Stable distinguished colours of several 3d metal complexes with DEAAnG, a typical ketoanil of the series alone and alongwith thiourea aroused our interest to undertake this work. Although all the three chromatographic methods could be used to resolve various quaternary mixtures, the TLC method showing the best resolution has been used in the quantitative analysis of mixtures of complexes; chromatogram fragments have been estimated spectrophotometrically.

The relationship between characteristic infrared frequencies of DEAAnG (primary ligand) in complexes and their migration rate has also been studied.

EXPERIMENTAL

Synthesis of p-diethylaminoanil of antraceneglyoxal and complexes

p-Diethylaminoanil of anthraceneglyoxal was synthesized by the reported method[4]. Simple complexes were prepared by mixing DEAAnG with metal chlorides in stoichiometric ratios in alcohol or acetone medium. Solids were isolated either by evaporating the reaction mixture or by increasing its pH with NaOH solution (in case of Ti(IV) complex only). Products were finally washed with ether. Mixed ligand complex were prepared by mixing simple complexes and thiourea in stoichiometric ratios in acetone. Reaction mixtures were evaporated on water bath and solids were washed with water and ether successively. All complexes were dried in hot air oven. Products were recrystallized from acetone and finally dried over anhydrous calcium chloride at reduced pressure. Chemicals used in the synthetic work were B.D.H. or S.M. Laboratory reagents.

Analysis and Physical Measurements

I.R. spectra of the compounds were recorded in CsI medium on a Perkin Elmer grating infrared spectrophotometer model-577. Conductometric measurements were made with T~~H~~oshniwal conductivity bridge using a dip-type cell. Elemental analysis was performed by routine micro analytical methods at C.D.R.I., Lucknow (India). Total and ionic chlorine and metal contents were estimated at N.R.E.C. College, Khurja. Optical density of the solutions were measured with Bausch and Lomb Spectronic-20 spectrophotometer.

Preparation, Loading and Development of TLC Plates, 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[6] was used to spread the aqueous slurry on the plates. Sample solutions prepared in EtOH or Me_2CO were applied with fine capillaries on dry plates and development was 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 scrapped and eluted with $EtOH/Me_2CO$. Optical densities of the eluates were determined at the λ max of their solutes and concentrations of the complexes were then deduced from their respective calibration curves (optical density v/s concentration) prepared under similar conditions of solvent and temperature.

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

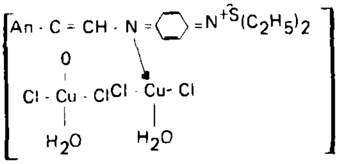
Electrochromatography was carried out in vertical type apparatus. Whatman No.1 paper strips (3x35 cm) were loaded at the centre by fine capillaries. Loaded strips were hanged with both ends in the electrode solvents and apparatus was closed. At saturation stage constant voltage was applied and after 2-35 hrs chromatograms were taken out and dried.

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

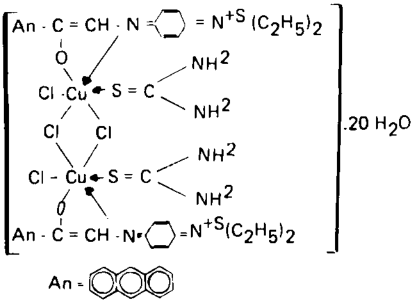
RESULTS AND DISCUSSION

Formulae of the complexes (Table-1) were deduced from their conductance and analytical data. Comparison of infrared spectra of ligands with their corresponding complexes revealed perturbation in C=O (1755 cm^{-1}), C=N (1695 cm^{-1}) frequencies of DEAAnG and C=S (1085 cm^{-1}) frequency of thiourea during complexation indicating their participation in coordination. Appearance of some new bands corresponding to M-O, M-N and M-S stretching also supports this inference. Metal-chloride coordinate bonding in complexes has also been identified. Considerable disturbance in the frequencies of 1:4 disubstitution (820 cm^{-1}) and aromatic C=C (1605, 1515, 1450cm^{-1}) of DEAAnG in complexes shows conjugation in the principal ligand, leading to the change of benzenoid structure to quinonoid while ligand interacted with metal ions. A typical complex structures are shown in figures.

$Cu^{(II)}$ · DEA AnG ·



$Cu^{(II)}$ - DEA AnG - (TU)



Chromatographic data obtained by migrating individual complexes revealed the separation of various quaternary mixtures of simple and mixed ligand complexes by TLC and PC, however, EC could resolve only ternary mixtures. Although, complex spots showed different migration rates in several solvents, only the solvents which could give best resolution of diverse complex mixtures have been noted in Table-2. Each complex migration has been found to be independent on the presence of others and on plate and paper size, however thickness of paper or layer has diverse effect on it.

The stretching frequency (ν) values (Table-1) of carbonyl and azomethine groups of primary ligand DEAAnG which are highly metal sensitive have been correlated with migration rates (Table-2)of the complexes in solvents giving best separation.TLC & EC migration rates of simple and mixed complexes in their mixtures are opposite to the orders in the values of ν (C=O). But migration rates of simple complexes in PC and EC and of mixed ligand complexes in TLC and PC which form identical orders are opposite to the sequence in ν (C=N). New chromatographic and spectroscopic (i.r.) correlation useful in making certain identification of resolved components form an interesting feature of the present study.

Although, various quaternary and ternary mixtures of simple and mixed ligand complexes could be resolved and identified (using chromatographic and spectroscopic correlations)

TABLE - 1

M.P. MOLAR CONDUCTANCE, ANALYSIS AND PRINCIPAL IR FREQUENCIES OF COMPLEXES

COMPLEX	M.P.	ΛM (Solvent/ electrolytic nature)	Elemental Analysis(%) Calcd.			
			C	H	N	Cl (ionic)
$[Ti(DEAAnG)_2Cl_2].2Cl$	175	155.22 (EtOH/1:2 electrolyte)	65.69 (65.48)	5.05 (4.92)	5.89 (5.68)	7.47 (7.38)
$[Mn(DEAAnG)_2(H_2O)_2]2Cl.5H_2O$	110	121.44 (Me_2CO/1:2 electrolyte)	61.66 (61.82)	6.12 (6.17)	5.53 (5.65)	7.01 (7.30)
$[Fe(DEAAnG)_2Cl_2].Cl$	140	70.33 (EtOH/1:1 electrolyte)	67.65 (67.55)	5.20 (5.35)	6.07 (6.15)	3.84 (3.92)
$[Co(DEAAnG)_2].2Cl$	110	162.87 (EtOH/1:2 electrolyte)	70.12 (70.25)	5.39 (5.60)	6.29 (6.53)	7.97 (7.88)
$[Cu_2(DEAAnG)Cl_4(H_2O)_2]$	125	7.37 (MeCN/non-electrolyte)	45.54 (45.20)	4.09 (4.35)	4.09 (4.33)	- -
$[Zn(DEAAnG)_2].2Cl.4H_2O$	140	189.20 (Me_2CO/1:2 electrolyte)	64.43 (64.55)	5.78 (5.75)	5.78 (5.90)	7.33 (7.50)
$[Fe(DEAAnG)(TU)Cl_3]$	130	13.20 (Me_2CO/non-electrolyte)	52.39 (52.60)	4.52 (4.51)	9.05 (9.12)	- -
$[Co(DEAAnG)_2(TU)_2].2Cl.8H_2O$	180	235.11 (Me_2CO/1:2 electrolyte)	54.64 (54.42)	6.07 (5.95)	9.44 (9.22)	5.98 (6.06)
$[Cu_2(DEAAnG)_2(TU)_2Cl_4].20H_2O$	135	37.60 (Me_2CO/non-electrolyte)	42.04 (42.25)	6.22 (6.12)	7.00 (7.15)	- -
$[Cd(DEAAnG)_2(TU)_2].2Cl.6H_2O$	210	220.22 (Me_2CO/1:2 electrolyte)	53.84 (53.60)	5.65 (5.55)	9.30 (9.20)	5.89 (6.02)

(Found)		Infrared frequencies (cm^{-1})									
Cl (Total)	M	C=O	C=N	C=C	1:4 Di-substitution	C=S	M-N	M-O	M-S	M-Cl	M-Cl-M
14.94 (15.08)	5.04 (5.19)	1630	1615	1515 1460	760	-	565	470	-	270	-
7.01 (7.30)	5.42 (5.28)	1715	1610	1515 1465	800	-	575	285	-	-	-
11.54 (11.44)	6.05 (6.10)	1705	1615	1515 1470 1450	800	-	560	470	-	300 280	-
7.97 (7.88)	6.62 (6.50)	1700	1665	1500 1470	810	-	530	450	-	-	-
20.72 (20.66)	18.54 (18.62)	1690	1615	1520 1475 1450	795	-	515	475	-	320	-
7.33 (7.50)	6.75 (6.60)	1620	1610	1520 1470	800	-	555	295	-	-	-
17.22 (17.00)	9.03 (8.98)	1725	1670	1610 1515 1460	820	1080	460	380	215	280 260	-
5.98 (6.06)	4.96 (5.00)	1720	1660	1605 1510 1460 1450	815	1075	530	445	280	-	-
9.21 (9.10)	9.24 (8.40)	1735	1620	1590 1510 1460 1445	790	1080	470	210	-	370	255
5.89 (6.02)	9.34 (9.50)	1725	1660	1610 1515 1450	815	1075	465	260 245	220	-	-

TABLE - 2

Resolving Solvents for Different Mixtures

Complexed Ligand(s)	Ions in Mixture	Resolving solvent	Chromatographic method of separation
DEAAnG	Cu(II) or Ti(IV) + Mn(II) or Fe(III) + Co(II) + Zn(II) (0.30) (0.38) (0.48) (0.52) (0.65) (0.75)	Me_2CO	T.L.C.
DEAAnG and T.U.	Cu(II) + Cd(II) + Co(II) + Fe(III) (0.08) (0.43) (0.50) (0.64)	n-BuOH-C_6H_5(1:1)	T.L.C.
DEAAnG	Cu(II)+/or Fe(III) + Ti(IV) + Mn(II) + Zn(II) (0.13) (0.22) (0.33) (0.45) (0.95)	$CHCl_3$	P.C.
DEAAnG	Fe(III) + Ti(IV) + Cu(II) + Mn(II) (0.00) (0.10) (0.24) (0.73)	Iso-BuCOMe	P.C.
DEAAnG and T.U.	Fe(III) + Cd(II) + Co(II) + Cu(II) (0.13) (0.21) (0.51) (0.92)		
DEAAnG	Co(II) or Fe(III) + Ti(VI) or Mn(II) + Zn(II) (1.6) (1.4) (2.2) (2.1) (3.0)	AcOH-$\frac{N}{10}$HCl([illegible]:1)	E.C.
DEAAnG and T.U.	Co(II) + Fe(III) or Cu(II) + Cd(II) (1.0) (1.8) (2.1) (3.0)	AcOH-$\frac{N}{10}$HCl(7:3)	E.C.

Values given in parenthesis are the R_F values.

TABLE - 3

Maximum Quantities of Complexes resolved by T.L.C. in their various mixtures

Mixture resolved	Spot colour	λmax	Weight of Complex applied on plate (μ)	Weight of Complex recovered (μ)	Error (%)
$[Cu_2(DEAAnG)Cl_4(H_2O)_2]$	Violet	470	65.00	64.50	-0.77
$[Mn(DEAAnG)_2(H_2O)_2].2Cl.5H_2O$	Pink	440	7.60	7.50	-1.30
$[Co(DEAAnG)_2].2Cl$	Reddish-Brown	420	46.00	45.75	-0.54
$[Zn(DEAAnG)_2]2Cl.4H_2O$	Gray	460	26.80	27.00	+0.75
$[Ti(DEAAnG)_2Cl_2].2Cl$	Blue	480	73.00	73.50	+0.68
$[Fe(DEAAnG)_2Cl_2].Cl$	Grayish--Brown	590	65.00	65.25	+0.38
$[Co(DEAAnG)_2].2Cl$			46.00	45.75	-0.54
$[Zn(DEAAnG)_2].2Cl.4H_2O$			26.80	27.00	+0.75
$[Cu_2(DEAAnG)_2(TU)_2Cl_4].2OH_2O$	Yellow	360	56.00	56.25	+0.45
$[Fe(DEAAnG)(TU)Cl_3]$	Reddish--Brown	460	59.50	59.25	-0.42
$[Co(DEAAnG)_2(TU)_2].2Cl.8H_2O$	Pink	430	21.60	21.75	+0.69
$[Cd(DEAAnG)_2(TU)_2].2Cl.6H_2O$	Pinkish-Gray	580	20.25	20.25	0.00

by all the three said methods (Table - 2), the quantitative separation, however, could only be achieved by TLC. The choice of TLC to PC and EC also lies in its quick resolution, compactedness of spots and high effectiveness of the solvents in it. Errors and limit of maximum separation have also been found out in several typical mixtures (Table-3). Several solvents showing vide difference in migration rates of the complexes indicated good possibility of their separations but owing to large diffusion and trailing effects they could not be used.

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