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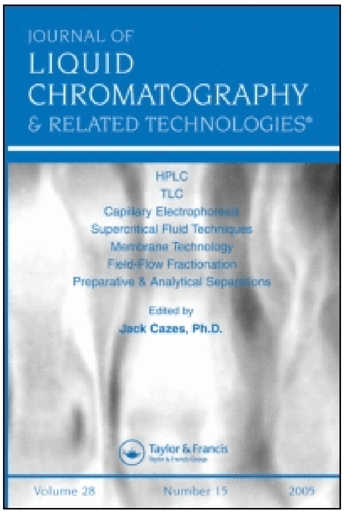

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THIN LAYER AND PAPER CHROMATOGRAPHIC SEPARATIONS OF d-BLOCK CATIONS COMPLEXED WITH ANILS

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ABSTRACT

Diverse binary, ternary and quaternary mixtures of Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II) and Au(III) d-block cations complexed with p-dimethylamino- and p-diethylamino- anils of thiophenoglyoxal have been separated by thin layer and paper chromatographic techniques. But quantitative separations have been done by thin layer chromatography, on account of wide difference in migration rates and high compectedness of complexes on gel layers. Chromatogram fragments visualised as such have been estimated spectrophotometrically.

INTRODUCTION

On account of rapid and better separability of organic compounds by paper and thin layer chromatography their metal complexes are chosen instead of metal ions as migrating species. Long persisting dark colours of organometal compounds leading to their self visualisation without any locating agent also justify their use in chromatographic analyses. Chromatographic analyses

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of cations complexed with variety of organic ligands[1-3] including ketoanils[4-8] are well documented. Thin layer and paper chromatographic separations of groups II, III and IV transitional basic radicals and their mixtures with Au(III) complexed with ketoanils including p-dimethylamino- and p- diethylamino anils of thiopheneglyoxal (abbreviated as DMATG and DEATG, respectively) unknown hitherto have been described in the present communication. Coloured complexes resolved by TLC have been estimated spectrophotometrically.

EXPERIMENTAL

Synthesis of Ketoanils and their Complexes :

Both ketoanils, DMATG and DEATG were prepared by condensing equimolar amounts of corresponding amine with 2-thiopheneglyoxal in chloroform; solvent was driven off at ∼ 60°C under reduced pressure. Residue was washed with small volume of ether several times and purified by recrystallization from chloroform.

Complexes were synthesized[10] by mixing metal chlorides and ketoanils in stoichiometric proportions in acetone-water or ethanol medium. Reaction mixtures were refluxed or concentrated and were left for crystallization. Dark crystalline products washed with ether and dried (∼ 60°C) were purified by recrystallization from methylcyanide, chloroform or dioxan.

Preparation, Loading and Development of TLC plates and P.C. Paper strips:

Silica gel G (BDH) mixed with starch (E. Merck, Darmstadt, G.F.R.) as binder (19:1, w/w) was used to prepare layers of 0.10cm thickness on glass plates of 18x3 cm and 18x10 cm sizes with a home-built apparatus[11]; coated plates were dried at ∼ 100°C in an oven. For the qualitative analysis 18x3 cm plates were loaded with sample solutions by fine capillaries but for quantitative analysis known volumes of standard solutions prepared by dissolving directly weighed quantities of complexes (and ligands) in methylcyanide, chloroform, acetone or alcohol were applied with micro pipette on 18x10 cm plates. While developing the plates in rectangular glass chambers by ascending technique migration of solvent front was kept constant at 8cms. On the chromatograms complexes were visualised as such. For quantitative estimations elutes of scrapped chromatogram fragments were made to 5.0 ml volume and their optical densities were determined spectrophotometrically at λmax of solutes. Elute concentrations were deduced from respective calibration curves prepared under similar conditions of temperature and solvent. For spectrophotometric measurements Bausch & Lomb spectronic-20 instrument was used.

In paper chromatography Whatmann No.1 15x3 cm paper strips loaded with the help of glass capillaries in 2-3 mm diameter spots were developed in cylindrical glass chambers by ascending technique. Solvent front was migrated to a constant distance of 8-10 cms.

Chemicals used in the synthetic work were BDH laboratory grade reagents. Analytical reagents were used in the chromatographic work.

RESULTS AND DISCUSSION

To look at the separation possibilities all the complexes were migrated individually on both, gel layers and paper strips, in several pure and mixture solvents. R_F values (Tables-1 & 2) obtained by migrating the complexes in their mixtures are conciding with R_F values of individually migrated spots. Interestingly, abnormally higher, migrations of almost all the complexes in benzene-pyridine mixtures having solvents ratios from 4:1 to 1:2 (v/v) in both chromatographic methods, than those in benzene or pyridine may be attributed to the substitution of chloro and/or aquo monoligands by pyridine in the coordination zone of metals.

Although, both the chromatographic (TLC and PC) methods are

TABLE - 1

QUALITATIVE SEPARATION OF COMPLEXED CATIONS OF DIFFERENT GROUPS

Metal Ions in complex mixture	Ligand in complex mixture	Spot Colour	λmax visible (nm)	TLC		PC	
				R_F	Resolving solvent	R_F	Resolving solvent
Hg(II)	DMATG	Pink gray	410	-	-	0.21	C_6H_6
Cu(II)		Dirty yellow	600			0.00	
Cd(II)		Buff	520			0.99	
Hg(II)	DEATG	Pink gray	390	0.85	MeCN	-	-
Cu(II)		Pink	490	0.02			
Cd(II)		Yellow gray	680	0.99			
Cr(III)	DMATG	Pink gray	395	0.18	C_6H_5N-C_6H_6 (1:9, v/v)	0.98	MeCN-H_2O-Proponal (3:5:1, v/v)

Fe(III)		Yellow	360	0.00		0.71	
Cr(III)	DEATG	Brown	370	0.78	AmOH	0.99	C_6H_6-$CHCl_3$ (2:1, v/v)
Fe(III)		Brown	355	0.95		0.15	or C_6H_6-Dioxan-H_2O (12:3:1, v/v)
Mn(II)	DMATG	Pink gray	525	-	-	0.25	C_6H_6-$CHCl_3$ (2:1, v/v)
Co(II)		Pink gray	375			0.00	
Ni(II)		Yellow	405			0.09	
Zn(II)		Brown gray	410			0.99	
Mn(II)	DEATG	Gray	410	0.76	BuOH	-	-
Co(II)		Gray	470	0.81			
Ni(II)		Pink gray	390	1.00			
Zn(II)		Yellow	510	0.86			

TABLE - 2

QUALITATIVE SEPARATION OF COMPLEXED Au(III) AND OTHER CATIONS

Metal ions in complex mixture	Ligand in complex mixture	TLC		PC	
		R_F	Resolving solvent	R_F	Resolving solvent
Au(III)	DMATG	0.42	Aq. BuOH-AcOH-$CHCl_3$ (5:2:5,v/v)	-	-
Cu(II)		0.00			
Ni(II)		0.85			
Zn(II)(orCr(III))		0.93(0.95)			
Au(III)	DMATG	0.00	$C_6H_5N-C_6H_6$ (3:7, v/v)	-	-
Zn(II) (or Cd(II))		0.65(0.64)			
Co(II)		0.79			
Fe(III)(or Cr(III))		0.95(0.96)			
Au(III)	DMATG	-	-	0.00	CCl_4
Hg(II)				0.09	
Co(II)				0.19	
Ni(II)(or Cr(III) or Fe(III)orZn(II) or Cd(II))				0.99(0.99)	
Au(III)	DMATG	-	-	0.15	BuOH-CCl_4-MeCN (3:3:1, v/v)
Cu(II)				0.50	
Fe(III)				0.69	

Cr(III)(or Co(II)orZn(II) or Cd(II) or Hg(II))				0.90(0.97 or 0.98)	
Au(III)	DEATG	0.06	MeCN	-	-
Co(II)(or Mn(II) or Hg(II))		0.84			
Fe(III)		0.92			
Ni(II)(or Cd(II) or Zn(II) or Cr(III))		0.98(or 0.99)			
Au(III)	DEATG	0.01	AmOH	-	-
Cu(II)		0.66			
Cr(III)(or Cd(II) or Hg(II))		0.78(0.77 or 0.79)			
Mn(II)(or Co(II) or Zn(II) or Fe(III))		0.90(0.89 or 0.98 or 0.95)			
Au(III)	DEATG	-	-	0.00	CCl_4
Mn(II)				0.07	
Ni(II)(or Cd(II))				0.15(0.18)	
Cr(III)(or Fe(III) or Co(II) or Zn(II))				0.99(0.99)	
Au(III)	DEATG	-	-	0.00	C_6H_6
Hg(II)(or Fe(III))				0.09(0.10)	
Co(II)				0.20	
Cd(II)				0.99	

Spot colours of Au(III)-DMATG and Au(III)-DEATG complexes are brown and orange, and λmax values are 420 nm and 400 nm, respectively.

TABLE - 3

QUANTITATIVE SEPARATION OF TYPICAL MIXTURES

Complex mixture	Weight of complex applied on plate (μg)	Weight of complex recovered (μg)	Error (%)	Resolving solvent
$Hg(DEATG)Cl_2.H_2O$	10.08	10.00	-0.8	MeCN
$Cu(DEATG)Cl.(OH)$	10.08	10.00	-0.8	
$Cd(DEATG)_2Cl_2$	17.60	17.50	-0.6	
$Cr(DMATG)Cl_3.4H_2O$	35.07	35.00	-0.2	$C_6H_5N-C_6H_6$ (1:9, v/v)
$Fe(DMATG)_2Cl_3$	60.12	60.25	+0.2	
$Mn(DEATG)_2Cl_2.2H_2O$	19.84	20.00	+0.8	BuOH
$Co(DEATG)Cl_2$	30.06	30.00	-0.2	
$Ni(DEATG)_2Cl_2$	22.80	22.75	-0.2	
$Zn(DEATG)Cl_2.2H_2O$	8.80	8.75	-0.6	
$Au(DEATG)Cl_3.3H_2O$	19.84	19.75	-0.5	AmOH
$Cu(DEATG)Cl(OH)$	10.08	10.00	-0.8	
$Cr(DEATG)Cl_3.4H_2O$	30.06	30.25	+0.6	
$Fe(DEATG)_2Cl_3$	30.06	30.25	+0.6	
$Au(DEATG)Cl_3.3H_2O$	9.92	10.00	-0.8	MeCN
$Co(DEATG)Cl_2$	30.06	30.00	-0.2	
$Fe(DEATG)_2Cl_3$	60.12	60.00	-0.2	
$Ni(DEATG)_2Cl_2$	22.80	23.00	+0.9	

Formulae of complexes have been reported in reference '10'.

equally effective in the qualitative separations of transitional basic radicals of II, III and IV groups (Table-1) and various mixtures of Au(III) with Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) (Table-2), TLC giving better quantitative separations than PC was applied in the quantitative analyses of typical mixtures. Maximum quantities of complexes in their mixtures resolved by this method have been noted against them in each mixture set (Table-3). Errors in estimations evidently show the high precision of the present method of TLC.

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