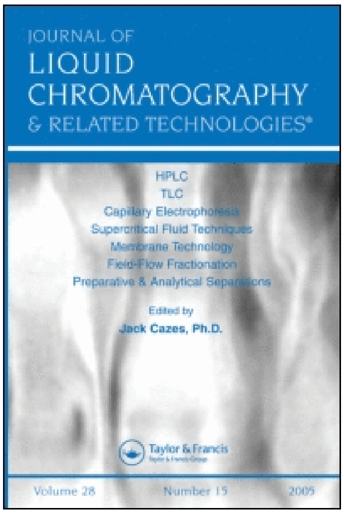

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Thin-Layer Chromatography of Metal Ions Complexed with Anils (V). Detection, Separation and Determination

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THIN-LAYER CHROMATOGRAPHY OF METAL IONS COMPLEXED WITH ANILS (V). DETECTION, SEPARATION AND DETERMINATION

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ABSTRACT

p-Diethylaminoanil of phenylglyoxal a bidentate ligand was used for complexation with Hg(II), UO_2(II), Au(III), Pt(IV) Mg(II), Bi(III), Sb(III) and Be(II) ions. The chelates were characterized by their analysis, molar conductance and infrared spectra. T.L.C. detection, separation and determination of these complexes on starch bound silica gel layers was studied Long persisting dark colour of the complexes rendered the spots self descernible and no locating agent was required. A maximum four complexes could be resolved and identified. Errors in determinations and maximum separation limits were also deduced.

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INTRODUCTION

The present communication is in continuation of our studies on the analytical applications of ketoanils(1-5) in the analysis of metal ions. Owing to lack of selectivity in the precipitation of metal ions p-diethylaminoanil of phenylglyoxal (6) {abbreviated as (DEAPG)} can not be used for the separation and determination of metals without using masking agents or controlling pH. The T.L.C. technique is used to resolve various mixtures of DEAPG complexes with Hg(II), UO_2(II), Au(III), Pt(IV) Mg(II), Bi(III), Sb(III) and Be(II) ions which have not been previously attempted although some references (6-8) on the synthesis and characterization of some of these complexes are available. New complexes were characterized by routine physicochemical methods.

The T.L.C. studies undertaken provide a simple and convenient method for the analysis of some inorganic mixtures and explore the possibility of detection and subsequent rapid separation, and estimation of the metals in different ores and minerals.

EXPERIMENTAL

Preparation of Solutions and Plates :

Solutions of metal chlorides (B.D.H. or J.M. London products) were prepared by dissolving their known quantities in alcohol. Metal chloride solutions were standardised (9) before use while ligand and complex solutions were used directly.

Glass plates (18x3 cm and 18x10 cm) were coated with silica gel freed from iron and chloride ions and mixed with starch (E. Merck) as binder (24:1, w/w) to prepare layers of

0.10 cm thickness by self designed apparatus (10). The coated plates were dried at ~100°C for 2-3 hrs in an oven. Dry loaded plates were developed in glass jars with ground-in-lids by ascending technique.

Isolation of Complexes :

Equimolar solutions of the reactants were mixed in stoichiometric ratio (ligand in slight excess); reaction mixtures were concentrated on water bath and products were crystallised out. Complexes were repeatedly washed with ether to remove unreacted ligand if any and recrystallised from acetone and dried on anhydrous calcium chloride under reduced pressure. Pt(IV) complex which precipitated out from the reaction mixture was washed with ether and dried in air oven. Pure dry products were analysed at C.D.R.I., Lucknow.

Physical Measurements :

Conductometric measurements on the alcoholic solutions of complexes were made with Toshniwal Conductivity bridge by dip-cell method. Infrared spectra were recorded in Nujol mull on 621-Perkin Elmer grating spectrophotometer and absorbance (O.D.) measurements were made with Bausch & Lomb 'Spectronic-20' spectrophotometer.

Procedure :

For qualitative studies, one or two drops of the test solutions were placed on plates with thin glass capillaries. After drying the spots development was made in different solvent systems and the ascent was fixed as 10cm in all cases; R_F values were measured as usual after detection. R_F values of the individual complexes were determined separately, by migrating pure complexes as well as by migrating metal ions after being complexed with ligand present in solvent (~ 0.02 gm/100ml). R_F values found by both methods for each complex were not appreciably differing. R_F values given in Table-2 are those obtained by migrating pure complexes.

For quantitative analysis several mixtures having different concentrations of resolvable component complexes were prepared and spotted on the plates (18x10 cm) with the help of micro pipette, and the development was performed in the chosen system. Chromatogram fragments were scrapped and complexes were eluted from the adsorbent with alcohol. The filtrates were evaporated and made to desired volume. Optical density of the elutes were determined spectrophotometrically at their λ max and concentrations in ppm were deduced from respective calibration curves prepared under similar conditions.

RESULTS AND DISCUSSION

Stoichiometry of the complexes in their solutions were found out spectrophotometrically following 'Mole-Ratio' method (11). Molecular formulae and structures of the chelates were established from analysis, molar conductance (12-14) and infrared (15-20) data (Table -1).

A perusal of TLC data revealed that addition of AcOH or water to BuOH decreased the movement of complexes, generally. Abnormally low R_F values obtained in BuOH-AcOH and BuOH-H_2O mixtures could be attributed (3,4,21,22) to the azeotropic properties of these mixture solvents. The effect of the layer thickness on R_F was also studied and it was found that layer thickness had the significant influence on the latter.

TABLE - 1

MOLECULAR FORMULA, ELECTROLYTIC NATURE AND PRINCIPAL I.R. FREQUENCIES OF COMPLEXES

Complex	Elemental Analysis Nitrogen(%) Calcd. (Found)	Analysis Metal(%) Calcd. (Found)	Molar Conductance Mhos/cm^2/mole (Electrolytic nature)	PRINCIPAL I.R. FREQUENCIES ν C=O	ν C=N	ν C=C (aromatic)	1:4 Di-substitution	ν M-N	ν M-Cl	ν M-O
DEAPG (I)	10.00 (9.81)	-	-	1692s	1660s	1605s	815s	-	-	-
PtL_2Cl_2 $Cl_2.6H_2O$	5.57 (5.58)	19.40 (19.18)	81.5 (1:2)	-	-	-	-	-	-	-
$AuLCl(H_2O)$ [illegible]$.Cl_2$	4.66 (4.90)	32.75 (32.34)	153.0 (1:2)	1650s	1660s	1550s	835m	-	-	-
$HgLCl(H_2O)$ $Cl.5H_2O$	4.09 (3.96)	30.41 (30.20)	37.4 (1:1)	1660m,sh	1592m	1575m	815m,b	540w	340w	404w
UO_2L_2 $Cl_2.6H_2O$	5.55 (5.40)	23.59 (23.36)	104.5 (1:2)	1660m,sh	1596s	1575m	815m,b	540m,b	-	420m,d
$BeLCl(H_2O)$ $Cl.3H_2O$	6.48 (6.60)	2.08 (2.00)	68.25 (1:1)	1668s	1608s	1556s 1540s	808s	552m	345w	400w
MgL_2Cl_2 $.6H_2O$	7.51 (7.23)	3.26 (3.18)	21.22 (Non-electrolytic)	1668s	1612s	1575s 1564s 1556s	815m	524w	-	420w
$Sb_2LCl_5(H_2O)_5$ $Cl.6H_2O$	3.00 (2.89)	26.04 (26.34)	49.0 (1:1)	1650s	1600s	- 1575s	832m	-	-	-
$Bi_2LCl_2(H_2O)_6$ $Cl_4.4H_2O$	2.48 (2.49)	37.09 (37.30)	327.4 (1:4)	1632s,b	1632s,b	1568s 1546s	832s	-	-	-

TABLE - 2

SPOT COLOUR, λ_{max} AND R_f OF THE COMPLEXES

Compound	Spot Colour	λ_{max} (nm)	BuOH	AcOH	BuOH--AcOH (2:1)	BuOH-AcOH (1:1)	BuOH--AcOH (1:2)	MeCN	Me_2CO	Me_2CO--$CHCl_3$ (2:1)	Aq.BuOH	Aq.BuOH--AcOH (2:1)	Aq.BuOH--AcOH (1:2)
Ligand (L)	Green	330	-	-	-	-	-	0.41	0.93	-	-	-	0.65
$[PtL_2Cl_2]Cl_2.6H_2O$	Light Pink	360	0.99	0.96	0.05	0.74	0.02	0.90	0.35	0.08	0.00	0.10	0.13
$[AuLCl(H_2O)]Cl_2$	Light Brown	360	0.99	0.99	0.98	0.74	0.97	0.99	0.45	0.11	0.00	0.00	0.00
$[HgLCl(H_2O)]Cl.5H_2O$	Pink	420	0.99	0.99	0.07	0.76	0.02	0.59	0.95	0.12	0.00	0.06	0.08
$[UO_2L_2]Cl_2.6H_2O$	Pink	360	0.99	0.00	0.08	0.76	0.99	0.97	0.88	0.17	0.00	0.00	0.00
$[BeLCl(H_2O)]Cl.3H_2O$	Light Brown	520	0.99	0.56	0.06	0.00	0.03	0.00	0.21	0.20	0.00	0.00	0.00
$[MgL_2Cl_2].6H_2O$	Brown	420	0.99	0.56	0.07	0.00	0.01	0.63	0.97	0.91	0.00	0.24	0.20
$[Sb_2LCl_5(H_2O)_5]Cl.6H_2O$	Light Yellow	520	0.99	0.97	0.99	0.78	0.97	0.63	0.35	0.18	0.00	0.00	0.00
$[Bi_2LCl_2(H_2O)_8]Cl_4.4H_2O$	Light Pink	520	0.99	0.98	0.96	0.72	0.98	0.00	0.25	0.11	0.00	0.06	0.00
Developing time (min.)			50	45	35	38	30	10	7	18	60	68	52

Room temperature = 37°C

TABLE - 3

QUANTITATIVE SEPARATIONS

Mixture Components	Amount of Complex loaded (μg)	Amount of Complex found (μg)	% Error
Mixture - 1			
$[MgL_2Cl_2].6H_2O$	9.9	10.0	+1.0
$[UO_2L_2]Cl_2.6H_2O$	55.2	55.0	-0.4
$[AuLCl(H_2O)]Cl_2$	40.2	40.0	-0.5
$[Bi_2LCl_2(H_2O)_8]Cl_4.4H_2O$	35.2	35.0	-0.6
Mixture - 2			
$[MgL_2Cl_2].6H_2O$	20.2	20.0	-1.0
$[UO_2L_2]Cl_2.6H_2O$	150.4	150.0	-0.3
$[PtL_2Cl_2]Cl_2.6H_2O$	132.2	132.5	+0.2
$[Bi_2LCl_2(H_2O)_8]Cl_4.4H_2O$	80.4	80.0	-0.5
Mixture - 3			
$[HgLCl(H_2O)]Cl.5H_2O$	22.4	22.5	+0.4
$[Sb_2LCl_5(H_2O)_5]Cl.6H_2O$	248.0	247.5	-0.2
$[BeLCl(H_2O)]Cl.3H_2O$	47.6	47.5	-0.2

R_F values of the complexes (Table -2) in Me_2CO and MeCN showed that various ternary and quarternary mixtures of the complexes could be resolved successfully. The R_F values with mixtures were found close to those obtained with single subs-tance. During the process of development it was also observed that spot colours in different mobile phases remained unchanged.

Quantitative separations of quarternary mixtures of Mg(II), UO_2(II), Au(III), Bi(III), and of Mg(II), UO_2(II), Pt(IV), Bi(III) complexes and ternary mixture of Hg(II), Sb(III), Be(II) complexes were performed in acetone using different concentrations of components. Maximum resolvable quantities of complexes in each mixture are noted in Table-3. The reproducibility of the results was checked on the same layers using the same solvent (Me_2CO) and it was observed that results were quite accurate and precise. Hence this method of TLC may be employed for the detection, separation and determination of all mentioned ions in micro amounts.

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