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

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NOTE

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. TLC detection, separation, and determination of these complexes on starch-bound silica gel layers were studied. Long persisting dark colors of the complexes rendered the spots self-descernible and no locating agent was required. A maximum of four complexes could be resolved and identified. Errors in determinations and maximum separation limits were also deduced.

INTRODUCTION

The present communication is in continuation of our studies on the analytical applications of ketoanil (*1–5*) in the analysis of metal ions. Owing to lack of selectivity in the precipitation of metal ions, *p*-diethylaminoanil of phenylglyoxal (DEAPG) (*6*) cannot be used for the separation and determination of metals without using masking agents or controlling the pH. The TLC 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 TLC studies undertaken provide a simple and convenient method

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for the analysis of some inorganic mixtures and explore the possibility of detection, 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 standardized (*9*) before use while ligand and complex solutions were used directly.

Glass plates (18 × 3 cm and 18 × 10 cm) were coated with silica gel freed from iron and chloride ions and mixed with starch (E. Merck) as a binder (24:1, w/w) to prepare layers of 0.10 cm thickness by a self-designed apparatus (*10*). The coated plates were dried at ~100°C for 2–3 h in an oven. Dry loaded plates were developed in glass jars with ground-in-lids by the ascending technique.

Isolation of Complexes

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

Physical Measurements

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

Procedure

For qualitative studies, 1 or 2 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 10 cm 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 the metal ions after they were complexed with the ligand present in the solvent ($\sim$0.02 g/100 mL). R_F values found by both methods for each complex were not appreciably different. The 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 (18 × 10 cm) with the help of a micropipette. Chromatogram fragments were scrapped, and complexes were eluted from the adsorbent with alcohol. The filtrates were evaporated and made to the desired volume. The optical densities of the elutes were determined spectrophotometrically at their λ_{max}, and concentrations in ppm were deduced from the respective calibration curves prepared under similar conditions.

RESULTS AND DISCUSSION

The stoichiometry of the complexes in their solutions were determined spectrophotometrically by using the "mole-ratio" method (*11*). Molecular formulas and structures of the chelates were established from analysis, molar conductance (*12–14*), and infrared (*15–20*) data (Table 1).

A perusal of T.L.C. data revealed that the addition of AcOH or water to BuOH generally decreased the movement of complexes. The 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.

The 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 to be close to those obtained with single substance. During the process of development it was also observed that spot colors 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. The maximum resolvable quantities of complexes in each mixture are noted in Table 3.

TABLE 1

Molecular Formula, Electrolytic Nature, and

Complex	Elemental analysis: Nitrogen (%) calc (found)	Elemental analysis: Metal (%) calc (found)	Molar conductance (mhos/cm²/mole) (electrolytic nature)
DEAPG (L)	10.00 (9.71)	—	—
$[PtL_2Cl_2]Cl_2 \cdot 6H_2O$	5.57 (5.58)	19.40 (19.18)	81.5 (1:2)
$[AuLCl(H_2O)]Cl_2$	4.66 (4.90)	32.75 (32.34)	153.0 (1:2)
$[HgLCl(H_2O)]Cl \cdot 5H_2O$	4.09 (3.96)	30.41 (30.20)	37.4 (1:1)
$[UO_2I_2]Cl_2 \cdot 6H_2O$	5.55 (5.40)	23.59 (23.36)	104.5 (1:2)
$[BeLCl(H_2O)]Cl \cdot 3H_2O$	6.48 (6.60)	2.08 (2.00)	68.25 (1:1)
$[MgL_2Cl_2] \cdot 6H_2O$	7.51 (7.23)	3.26 (3.18)	21.22 (Nonelectrolyte)
$[Sb_2LCl_5(H_2O)_5]Cl \cdot 6H_2O$	3.00 (2.89)	26.04 (26.34)	49.0 (1:1)
$[Bi_2LCl_2(H_2O)_8]Cl_4 \cdot 4H_2O$	2.48 (2.49)	37.90 (37.30)	327.4 (1:4)

TABLE 2

Spot Color, λ_{max} and

Compound	Spot color	λ_{max} (nm)	BuOH	AcOH	BuOH–AcOH (2:1)	BuOH–AcOH (1:1)
Ligand (L)	Green	330	—	—	—	—
$[PtL_2Cl_2]Cl_2 \cdot 6H_2O$	Light pink	360	0.99	0.96	0.05	0.74
$[AuLCl(H_2O)]Cl_2$	Light brown	360	0.99	0.99	0.98	0.74
$[HgLCl(H_2O)]Cl \cdot 5H_2O$	Pink	420	0.99	0.99	0.07	0.76
$[UO_2L_2]Cl_2 \cdot 6H_2O$	Pink	360	0.99	0.00	0.08	0.76
$[BeLCl(H_2O)]Cl \cdot 3H_2O$	Light brown	520	0.99	0.56	0.06	0.00
$[MgL_2Cl_2] \cdot 6H_2O$	Brown	420	0.99	0.56	0.07	0.00
$[Sb_2LCl_5(H_2O)_5]Cl \cdot 6H_2O$	Light yellow	520	0.99	0.97	0.99	0.78
$[Bi_2LCl_2(H_2O)_8]Cl_4 \cdot 4H_2O$	Light pink	520	0.99	0.98	0.96	0.72
Developing time (min) Room temperature = 37°C			50	45	35	38

Principal IR Frequencies of Complexes

Principal IR frequencies						
$\nu_{C=O}$	$\nu_{C=N}$	$\nu_{C=C}$ (aromatic)	1:4 Disubstitution	ν_{M-N}	ν_{M-Cl}	ν_{M-O}
1692s	1660s	1605s	815s	—	—	—
—	—	—	—	—	—	—
1650s	1660s	1550s	835m	—	—	—
1660m, sh	1592m	1575m	815m, b	540w	340w	404w
1660m, sh	1596s	1575m	815m, b	540m, b	—	420w, d
1668s	1608s	1556s 1540s	808s	552m	345w	400w
1668s	1612s	1575s 1564s 1556s	815m	524w	—	420w
1650s	1600s	— 1575s	832m	—	—	—
1632s, b	1632s, b	1568s 1540s, b	832s	—	—	—

R_F of the Complexes

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)
—	0.41	0.93	—	—	—	0.65
0.02	0.90	0.35	0.08	0.00	0.10	0.13
0.97	0.99	0.45	0.11	0.00	0.00	0.00
0.02	0.59	0.95	0.12	0.00	0.06	0.08
0.99	0.97	0.88	0.17	0.00	0.00	0.00
0.03	0.00	0.21	0.20	0.00	0.00	0.00
0.01	0.63	0.97	0.91	0.00	0.24	0.20
0.97	0.63	0.35	0.18	0.00	0.00	0.00
0.98	0.00	0.25	0.11	0.00	0.06	0.00
30	10	7	18	60	68	52

TABLE 3

Quantitative Separations

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

The reproducibility of the results was checked on the same layers using Me_2CO as solvent, and it was observed that the results were quite accurate and precise. Hence this method of T.L.C. may be employed for the detection, separation, and determination of all the above-mentioned ions in micro amounts.

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REFERENCES

1. R. K. Upadhyay and R. C. Saxena, *J. Indian Chem. Soc.*, *50*, 158 (1973).
2. R. K. Upadhyay, R. Prasad, and S. C. Sharma, *Ibid.*, *51*, 528 (1974).
3. R. K. Upadhyay and R. R. Bansal, *Ibid.*, *53*, 15 (1976).
4. R. K. Upadhyay and V. P. Singh, *Ibid.*, *52*, 1164 (1975).
5. R. K. Upadhyay and V. P. Singh, *Ibid.*, *54*, 495 (1977).
6. H. P. S. Verma, PhD Thesis, Meerut University, Meerut, India, 1975.
7. M. L. Singhal, PhD Thesis, Meerut University, Meerut, India, 1976.
8. R. K. Upadhyay, M. L. Singhal, A. K. Saxena, and R. Prasad, *Acta Chim.*, *83*, 299 (1974).
9. A. I. Vogel, *A Text Book of Inorganic Quantitative Analysis*, 3rd ed., Longmans, London, 1962.
10. E. Stahl, *Thin Layer Chromatography*, 2nd ed., Springer, Berlin, 1966.

11. J. H. Yoe and A. L. Jones, *Ind. Eng. Chem., Anal. Ed., 16*, 111 (1944).
12. S. M. F. Rahman, J. Ahmed, and M. M. Haq., *J. Inorg. Nucl. Chem., 35*, 3351 (1973).
13. M. M. Jones, *Elementary Coordination Chemistry*, Prentice-Hall, Englewood Cliffs, New Jersey, 1964.
14. W. J. Geary, *Coord. Chem. Rev., 7*, 81 (1971).
15. J. R. Dyer, *Applications of Absorption Spectroscopy of Organic Compounds*, Prentice-Hall of India, New Delhi, 1969.
16. C. N. R. Rao, M. V. George, J. Mahanty, and P. T. Narasimhan, *A Hand Book of Chemistry and Physics*, East-West Press, New Delhi, 1967.
17. R. N. Saxena and K. K. Pandey, *J. Indian Chem. Soc., 49*, 782 (1972).
18. G. S. Shaphard and D. A. Thornton, *Helv. Chim. Acta, 54* 2212 (1971).
19. K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, Wiley, New York, 1968.
20. J. P. Fackler, *Prog. Inorg. Chem., 7*, 361 (1966).
21. R. K. Upadhyay, V. P. Singh, and U. Bajpai, *J. Chromatogr., 93*, 494 (1974).
22. R. K. Upadhyay, U. Bajpai, and R. R. Bansal, *Monatsh. Chem., 107*, 1221 (1976).

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