Thin –layer Chromatography of Isomeric Complexes of Ambidentate Ketoanil Ligands: Separation, Detection and Effect of Chelate Ring Contraction on R_F Values

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ABSTRACT

Complexes of Cu(II) nitrate and chloride salts with p-chloro-, p-bromo-and p-iodo-anils of 2-thiophene glyoxal, isolated as binary mixtures of isomers, were separated on thin-layers of silica gel. Separation of mixtures in bulk and of their known quantity was done by column chromatography for determination of isomeric composition of isolates. Resolved isomers were identified using correlation of their R_F with spectral properties. The effect of chelate ring contraction on R_F values has also been investigated.

Key words: Thin layer chromatography, column chromatography, ambidentate ligands, Ketoanils, chelates.

INTRODUCTION

Although thin- layer chromatography (TLC), being superior to other techniques in providing rapid and better separation , is used in routine in testing homogeneity, resolution and identification of organic and inorganic compounds as one of the classical methods but mechanistic aspects of analytes migration and diverse interactions of properties of solvents and analytes are usually ignored. Moreover TLC reports on isomeric species generally pertain to organic compounds whereas inorganic isomers [1-3] including complexes of ketoanils [4,5]find little mention in literature. The lack of knowledge on analytical chemistry of isomeric inorganic compounds in general, and of isomeric complexes of ketoanils in particular, tempted us to carry out chromatographic analyses of binary mixtures of isomeric complexes synthesized by Cu(II) chloride and nitrate salts with three ambidentate ligands , 2-thiophene glyoxal-p-chloro-, -p-bromo-and –p-iodo-anils abbreviated as TGCA, TGBA and TGIA respectively, which has not been reported hitherto.

EXPERIMENTAL

Preparation and bulk separation of isomeric complexes

Isolation, stoichemetries and structures of isomeric complexes have been reported in our previous communication [6]. Separation of binary isolates in bulk was by column chromatography using silica gel adsorbent and benzene developer. Component 'a' of each pair of isomers is slow moving (low R_F) and 'b' is fast moving (high R_F).

Loading and development of TLC plates

Glass plates (20 × 20) coated with silica gel (Merck. KGaA) were used for TLC work. TLC plates were activated by heating at ~ 60 °C to ensure compactness of spots before use. Sample solutions in acetone were spotted on warm plates with fine capillaries in series on a line 2 cm from the lower edge of the plates. The oven dried loaded plates were developed in rectangular glass chambers with ground –in- lids presaturated with developing solvent by ascending technique to obtain reproducible results. When the development had proceeded for 8cm the plates were removed from the chamber and the development time was noted. Owing to dark colours of spots of analytes they were discernible in day light.

Quantitative separation and estimation

Taking advantage of wide difference in R_F values (Table-1) of components of binary mixtures in benzene (low R_F, 0.00 and high R_F , 0.91-0.95), solutions of binary isolates in acetone containing 200 mg of each were separated by column chromatography conducted in column (50 cm length an 3cm diameter) containing silica gel (~ 65 mesh, BDH) adsorbent. Eluates of fast moving -b (high R_F) eluted with benzene and slow moving –a (low R_f) eluted with MeCN were evaporated at ~ 50 °C under reduced pressure and weighed to calculate isomeric composition of binary mixtures (Table-2). The same experiment was conducted three times.

RESULTS AND DISCUSSION

All the non- electrolytic complexes are four coordinate in square planar stereochemistry involving quininoid structure of ligands. Five membered chelate ring of chloro and nitrato Cu(II)-

TGCA, Cu(II)-TGBA-a and Cu(II)-TGIA-a complexes is comprised of carbonyl oxygen and azomethine nitrogen atoms whereas chelate ring of $CuCl_2$- TGBA-b, $Cu(NO_3)_2$- TGBA-b, $CuCl_2$- TGIA-b and $Cu(NO_3)_2$- TGIA-b isomers is composed of carbonyl oxygen and thienyl sulfur [7,8] (Fig.1).

Thin layer chromatographic development of all the binary isolates and their resolved individual components was carried out in ten solvent systems and R_F values were found the same (Table 1). Although all the solvents, except Me_2CO, MeCN and toluene, showed good resolving capacity for binary mixtures of isomeric complexes but best separation could be achieved in benzene.

Para substituents of ligands being electron repellent some electron density is transferred from them to carbonyl oxygen, leading to change from benzenoid to quininoid structure of ligands. The magnitude of this charge on carbonyl oxygen, related directly with electron repelling ability of para substituent of ligands, predominantly govern the metal-oxygen bond strength. The size of the chelate ring, however, is determined by strength of bonds, metal-oxygen and metal-nitrogen bonds, and metal-oxygen and metal-sulphur bonds in low R_F and high R_F complexes respectively.

In $CuCl_2$-TGCA, Cu $(NO_3)_2$ _TGCA, $CuCl_2$— TGBA (a), $Cu(NO_3)_2$TGBA (a),$CuCl_2$-TGIA (a) and $Cu(NO_3)_2$- TGIA (a) complexes υCu-O and υCu-N frequencies falling in the order of electron repelling ability of para substituent of ligands, Cl (TGCA) > Br (TGBA) > I (TGIA), clearly reveal chelate ring contraction in the order of IR parameters. The R_f values (Table 1) have also been found to follow the same order as to that in chelate ring contraction or spectral parameters in all the solvents except MeCN which showed opposite R_F order to spectral parameters probably due to its highest polarity among other solvents used[9-11].

In high R_F (b) complexes of TGBA and TGIA υCu-O and υCu-S frequencies follow the order, Br (TGBA) ≥ I (TGIA), corresponding to electron repelling ability of para substituent, electron density on carbonyl oxygen of ligands or chelate ring contraction. The R_F values of these complexes follow the identical order to IR parameters or chelate ring

Table 1: Thin layer chromatography of ketoanils and their complexes; spot colour, R_F and M-L bond frequencies (cm^{-1})

Complexes	Spot colour	RF×100										M-L bond frequencies(cm^{-1})		
		Me OH	Et OH	Pr OH	Bu OH	Et$_2$O	Me$_2$cO	Me CN	CHCl$_3$	C$_6$H$_6$	C$_6$H$_5$ CH$_3$	νM-S	νM-O	νM-N
TGCA	Light brown	80	92	89	84	62	94	94	34	56	00	-	-	-
Cu(TGCA)Cl$_2$	Gray	92	94	82	44	00	94	93	00	00	00	-	524d	431
Cu(TGCA)(NO$_3$)$_2$	Gray brown	88	92	76	77	00	94	92	00	00	00	-	530	425
TGBA	Light brown	87	89	82	86	77	94	93	49	57	27	-	-	-
Cu(TGBA)Cl$_2$,H$_2$O,a	Gray	00T	00	00	00	00	90	96	00	00	00	-	508	412
Cu(TGBA)Cl$_2$,3H$_2$O,b	Cannary yellow	64	78	71	74	77	94	96	83	91	00	238	525	-
Cu(TGBA)(NO$_3$)$_2$.3H$_2$O,a	Gray	00T	00	00	00	00	90	96	00	00	00	-	525	425
Cu(TGBA)(NO$_3$)$_2$,b	Cannary yellow	62	74	76	64	76	90	96	85	91	00	249	482	-
TGIA	Light brown	84	93	89	80	76	94	95	48	51	28	-	-	-
Cu(TGIA)Cl$_2$,3H$_2$O,a	Gray brown	00T	00	00	00	00	94	98	00	00	00	-	496	411
Cu(TGIA)Cl$_2$,b	Cannary yellow	57	76	64	67	81	94	98	97	95	00	240d	525	-
Cu(TGIA)(NO$_3$)$_2$,a	Gray brown	00T	00T	00	00	00	97	00	00	00	00	-	525	405
Cu(TGIA)(NO$_3$)$_2$,b	Cannary yellow	59	72	63	67	85	94	97	95	95	00	250	475	-
Development time (min) 25		27	45	60	30	9	19	20	22	24				

Table 2: Isomeric composition of binary mixtures

Mixture of components resolved	Amount of mixture applied(mg)	Amount of mixture components recovered(mg)	% Eror	Isomeric compositio n
$Cu(TGBA)Cl_2.H_2O$ (a) $Cu(TGBA)Cl_2.3H_2O$ (b)	200	138 57	2.5%	121:50
$Cu(TGBA)(NO_3)_2.3H_2O$ (a) $Cu(TGBA)(NO_3)_2$ (b)	200	156 42	1:1%	371:100
$Cu(TGIA)Cl_2.3H_2O$ (a) $Cu(TGIA)Cl_2$ (b)	200	100 100	0:0%	1:1
$Cu(TGIA)(NO_3)_2$ (a) $Cu(TGIA)(NO_3)_2$(b)	200	140 58	1.0%	241:100

The amounts of mixture components recovered are the mean values of three experiments
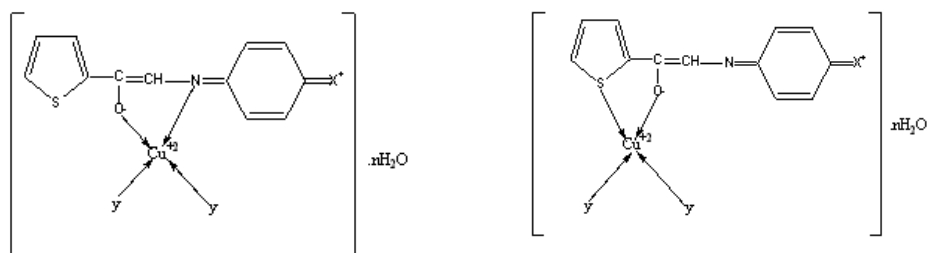
Where X= Cl, Br or I and Y= Cl⁻ or NO_3^- ; n=0,1 or 3

Fig. 1(a) Is a-isomer and **(b)** is b-isomer

contraction in alcohols but in other solvents, whether oxygen-containing or non-oxygen containing opposite R_F order to IR sequence is obtained for the reason unknown as yet.

Both isomers in their mixtures on resolution could be identified by using correlation of metal-ligand bonds frequencies, and R_F values in their resolving solvents.

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