

CHAPTER III :

MATERIALS AND METHODS.

## A. Materials :

Most of the compounds used in these investigations were prepared by well known methods. In Tables 3.1 - 3.6 therefore are given only the preparative references and relevant characterisation data of the compounds.

A few new compounds were synthesised during the course of these studies. Of these compounds the mixed chelate picolinate mono (biguanide) copper(II) is considered important. Details about the characterisation and properties of these new compounds are included in this section.

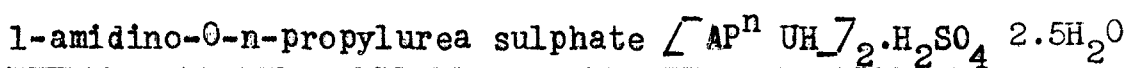
### Bis(1-amidino-0-n-propylurea) copper(II) chloride :

Copper(II) chloride dihydrate (2g), dicyandiamide (2g) and n-propyl alcohol (25 ml) were refluxed for 6 hours on a water bath. The violet solution was filtered and allowed to stand in the refrigerator for one or two days when rose-violet crystals separated. These were filtered by suction and recrystallised either from hot water or hot ethanol and dried in air. Yield 2.5 gms. Characterisation data are given in Table 3.4.

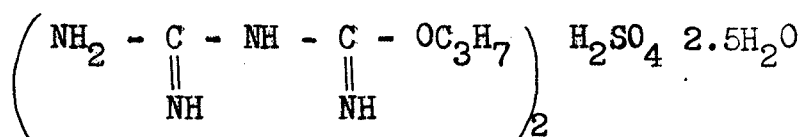
### Bis(1-amidino-0-n-amylurea) copper(II) chloride :

This was obtained by refluxing copper(II) chloride dihydrate (2g), dicyandiamide (2g) in n-amyl alcohol (25 ml) for

8 hours on a water bath when a violet solution was obtained. This was filtered and the filtrate kept in the refrigerator for two days. The rose violet crystals were collected and were recrystallised from hot ethanol and finally dried in air. Yield 3 gms. Characterisation data are given in Table 3.4.



Copper(II)

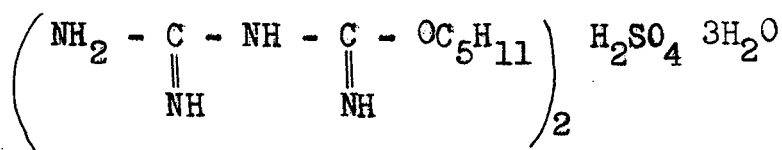


Copper(II) complex,  $\left[ \text{Cu}(\text{AP}^{\text{n}}\text{UH})_2 \right] \text{Ac}_2$ , was obtained by refluxing dicyandiamide (25 g), copper(II) acetate (25 g) and n-propyl alcohol (250 ml). The complex acetate was recrystallised from ethanol. The pure complex acetate was then dissolved in ethanol and treated with an aqueous solution of ammonium sulphate when dark rose-red complex copper(II) sulphate was precipitated. This was filtered and washed with water. The washed residue was then suspended in water (150 ml), copper removed by  $\text{H}_2\text{S}$  and excess  $\text{H}_2\text{S}$  was freed by passing air through it. The filtrate was then concentrated to about 50 ml on a steam bath and then cooled in ice. To this excess acetone was then added with stirring when white crystalline precipitate was obtained.

The sulphate is extremely soluble in water and sparingly soluble in ethanol but is insoluble in acetone. The sample was dried over  $\text{CaCl}_2$  at room temperature. Yield 23 gms.

Analysis : Found N, 13.0; SO<sub>4</sub>, 22.12; H<sub>2</sub>O, 10.5  
 $\left[ \text{AP}^{\text{nUH}} \right]_2 \text{H}_2\text{SO}_4 \cdot 2.5 \text{H}_2\text{O}$  requires N, 12.99; SO<sub>4</sub>, 22.26 and H<sub>2</sub>O, 10.4 per cent.

1-amidino-O-n-amylurea sulphate  $\left[ \text{AA}^{\text{nUH}} \right]_2 \cdot \text{H}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$  :



This was obtained from n-amylalcohol (250 ml), copper(II) acetate (25 g) and dicyandiamide (25 g) as described above for the n-propyl derivative. Yield 16 gms.

Analysis : Found N, 11.17; SO<sub>4</sub>, 19.25; H<sub>2</sub>O, 10.53  
 $\left[ \text{AA}^{\text{nUH}} \right]_2 \cdot \text{H}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$  requires N, 11.24; SO<sub>4</sub>, 19.27; H<sub>2</sub>O, 10.84 per cent.

Bis(1-amidino-O-n-propylurea) nickel(II) chloride :

An aqueous solution of 1-amidino-O-n-propylurea sulphate (2.5g) and nickel sulphate (1.2g) was made strongly alkaline when a yellow complex nickel base precipitated out. This was filtered and washed several times with water till free from alkali. The complex nickel base was then triturated with dil (2 N) HCl till neutral to litmus and the product was recrystallised from ethanol. It forms bright orange yellow crystals. Characterisation data<sup>are</sup> given in Table 3.4.

The chemical properties, magnetic moments, electrical conductance and electronic spectra of the above 1-amidino-O-n-propyl/n-amylurea complexes of copper(II) and nickel(II) are very similar to the already known 1-amidino-O-alkylurea compounds reported from this laboratory since 1959. For brevity it may only be mentioned that the above copper(II) chelates show an absorption maxima around 19 kK which is typical of square planar  $\left[ \text{Cu N}_4 \right]$  chromophore<sup>226-230</sup> while nickel(II) complexes are diamagnetic and have absorption band around 23 kK characteristic of square planar  $\left[ \text{Ni N}_4 \right]$  chromophore<sup>244,254,255</sup>.

Picolinato mono(biguanide) copper(II) chloride :

A few copper(II) mixed chelates containing a biguanide alongwith a bidentate (or a tridentate) amino acid or a bidentate heterocycle like dipyridyl or o-phenanthroline have been reported in the literature<sup>250-253</sup>. In continuation of these investigations we now describe the synthesis and properties of picolinato mono (biguanide) copper(II) chloride.

Experimental :

Synthesis : Biguanide acid sulphate mono hydrate<sup>256</sup> (1.8 g) was dissolved in hot water (25 ml) and treated with an aqueous solution of barium chloride dihydrate (3 g in 10 ml). The mixture was digested on a steam bath for 40 minutes and then filtered. The clear filtrate was treated with an aqueous solution of cupric chloride dihydrate (1.36 g in 10 ml). The pH of the solution was adjusted to  $\sim 6$  with dilute  $\text{NH}_4\text{OH}$  when a deep blue solution

was obtained. To this blue solution, picolinic acid<sup>257</sup> (0.96 g in 10 ml, the pH of which was adjusted to 7 with dilute  $\text{NH}_4\text{OH}$ ) was added. A blue violet somewhat gelatinous precipitate immediately separated. The precipitate was allowed to stand at room temperature for 30 minutes and then filtered. The precipitate was then digested with water ( $\sim 80$  ml) on a steam bath for one hour and filtered from an insoluble residue of bis(picolinato)copper(II). The solution was allowed to stand on the steam bath for an additional one hour and then allowed to stand over night at room temperature. The beautiful deep blue shining crystals were then collected, washed with ice cold water and dried in air. Yield 0.8 g.

[Found Cu, 19.7; N, 26.3; Cl, 10.9  $\text{[Cu(BigH)(pic)]Cl}$   
requires Cu, 19.7; N, 26.2 and Cl, 11.0 per cent.]

The above procedure appeared essential in order to obtain well formed crystals. The compound is soluble in water but insoluble in other common solvents.

Conductance was measured at  $25^\circ\text{C}$  in aqueous solution with a Phillips Conductivity Bridge type PR 9500. Equivalent weight was determined by passing an aqueous solution of the complex through an ion exchange column (IR - 120;  $\text{H}^+$  form) and by eluting with sufficient water. The liberated acid was then titrated with a standard alkali solution. Solution spectrum was run in water with the help of an UVISPEK spectrophotometer using 1 cm cells. Reflectance spectrum was obtained in a Carl Zeiss PMQ II

spectrophotometer through the courtesy of Dr.L.F.Lindoy and Dr.G.M.Mocler. Infra red spectrum was obtained on a Perkin Elmer equipment at the University College of Science, Calcutta.

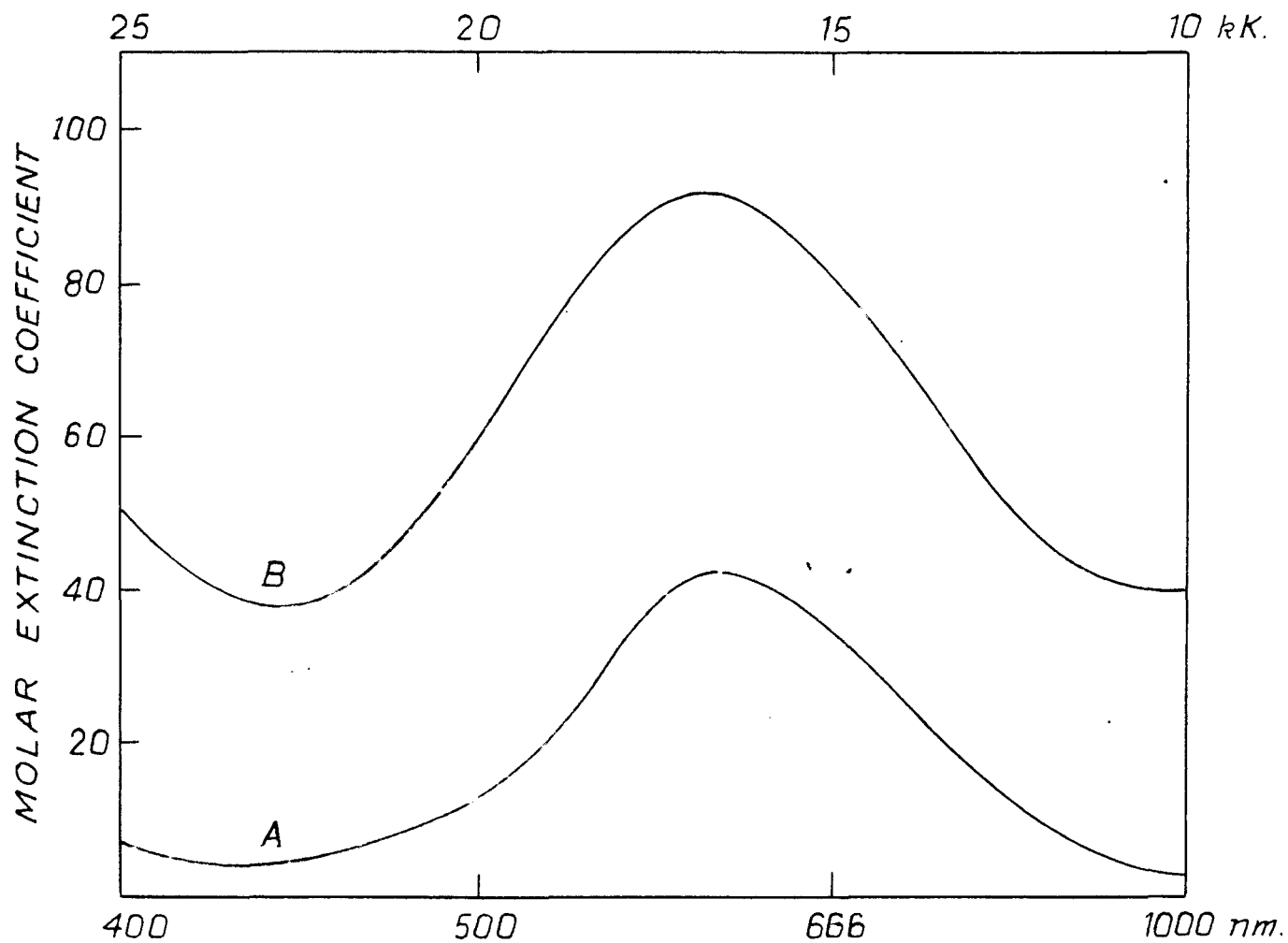
### Results and Discussion :

At about pH~6, copper(II) biguanide system provides an equilibrium between mono(biguanide) copper(II) and bis(biguanide) copper(II)<sup>221,250</sup>. Addition of neutralised picolinic acid provides a crude voluminous precipitate which contains the mixed chelate  $\left[ \text{Cu}(\text{pic})(\text{BigH}) \right] \text{Cl}$  alongwith  $\left[ \text{Cu}(\text{pic})_2 \right]$ . On crystallisation from hot water the mixed chelate alone goes into solution while bis(picolinato) copper(II) is left behind. On proper digestion on a steam bath followed by slow crystallisation at room temperature the mixed chelate is obtained in the form of beautiful shining blue crystals. The crystals appear under the microscope as a single homogeneous species rather than as a mixture of  $\left[ \text{Cu}(\text{BigH})_2 \right] \text{Cl}_2$  and  $\left[ \text{Cu}(\text{pic})_2 \right]$ . The bromide and the iodide salts could not be obtained in a state of satisfactory purity. The aqueous conductance of  $99 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$  is typical of a uni-univalent electrolyte<sup>258</sup>. The equivalent weight (Found, 318; required, 321) supports the analytical results as also the conductivity finding. The magnetic moment value for this compound was found to be 1.91 BM ( $\chi_g = 4.102 \times 10^{-6}$ ;  $\chi_M(\text{corr}) = 1500 \times 10^{-6}$ ). The infra red spectrum shows bands characteristic of biguanide<sup>253</sup> (NH stretch at  $3300 \text{ cm}^{-1}$ ) while C = N stretch and coordinated carboxyl stretch appear together around 1650. Aromatic vibration appears

at  $1545\text{ cm}^{-1}$  in conformity with reported values. In this connection it may be mentioned that the C = N stretch of  $\left[\text{Cu}(\text{BigH})_2\right]\text{Cl}_2$  is known to appear at  $1645\text{ cm}^{-1}$  while coordinated carboxyl appears around  $1645\text{ cm}^{-1}$  for picolinic acid<sup>249,253,259,260</sup>.

The electronic spectrum in the solid as also in aqueous solution registers a single, nearly symmetrical band centred around 600 nm (16.7 kK) ( $\epsilon = 42$ ) (Fig. 3.1). The most interesting feature is that the spectral profile as also the band position remain invariant in solid state and in aqueous solution indicating the persistence of the same chromophore in both the states. This spectral behaviour alongwith the fact that the compound crystallises from aqueous solution in anhydrous state strongly suggest a square planar or an extremely tetragonal  $\left[\text{Cu N}_3\text{O}\right]$  chromophore. A four coordinate tetrahedral structure is immediately ruled out in view of the comparatively high absorption band and recognised high field character of biguanide<sup>248,249</sup> and picolinic acid<sup>260,261</sup>. Had the complex assumed a distorted octahedral  $\left[\text{Cu N}_3\text{O}_3\right]$  chromophore in aqueous solution through coordination of two water molecules we would have observed a large shift to lower energy from that in the solid state. A dimeric or polymeric five coordinate structure,  $\left[\text{Cu N}_3\text{O}_2\right]$ , can be written for the complex in the solid state but the spectral profile does not look like such a species. All five coordinate species for example  $\left[\text{Cu}(\text{O-O})(\text{N-N-O})\right]$ <sup>262</sup>,  $\left[\text{Cu}(\text{dien Me})\text{Cl}_2\right]$ <sup>263</sup>,  $\left[\text{Cu}(\text{tren Me})\text{X}\right]\text{X}$ <sup>264</sup>, (X = Br,  $\text{ClO}_4$ )  $\left[\text{Cu}(\text{tfac DPT})\right]$ <sup>265</sup>,  $\left[\text{Cu}(\text{o-phen})_2\text{CN}\right]$ <sup>266</sup> etc. (where, O-O = salicylaldehyde (sal) anion and 2-hydroxyacetophenone (hac)





*ELECTRONIC SPECTRA OF  $[\text{Cu}(\text{pic})(\text{BigH})]\text{Cl}$*

*Fig.3'1. A, in aqueous solution*

*B, reflectance (arbitrary scale)*

anion; N-N-O = Schiff Base derived from sal and  $\text{NH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NR}_2$  and also hac and  $\text{NH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NR}_2$ ; tren Me = tris(2-dimethyl aminoethyl) ammine; tfac DPT = Schiff Base from trifluoroacetyl acetone and bis(3,3'-amino propyl ammine) are characterised by an absorption band alongwith a prominent shoulder in the range 10 kK to 16 kK. Moreover these five coordinate species are characterised by a significantly high molar extinction coefficient ( $\epsilon = 200$ ) at the absorption maxima. It may be pointed out here that a distorted octahedral  $[\text{Cu}(\text{H}_2\text{O})(\text{Big})(\text{IDA})]$  (chromophore  $[\text{Cu} \text{N}_3 \text{O}_3]$ ) in aqueous solution shows an absorption band centred around 13.6 kK (735 nm), ( $\epsilon = 95$ ) while  $[\text{Cu}(\text{H}_2\text{O})(\text{dipy})(\text{IDA})]$  absorbs at 15.1 kK ( $\epsilon = 57$ )<sup>253</sup>. (Table 3.1).

There are but a limited few square planar copper(II) complexes with the  $[\text{Cu} \text{N}_3 \text{O}]$  chromophore. One such complex is  $[\text{Cu}(\text{succin})(\text{py})(\text{H}_2\text{O})]$  absorbing at 520-540 nm (18.5-19.2kK) in the solid state<sup>224</sup>. This compound, however, shifts its spectrum to lower energy indicating a distorted octahedral  $[\text{Cu} \text{N}_3 \text{O}_3]$  configuration. The solid state spectrum of square planar bis(picolinato) copper(II) (chromophore  $\text{CuN}_2\text{O}_2$ ) shows bands at 600 nm (16.7 kK), which assumes a distorted octahedral structure in aqueous solution, absorbing band shifting to 640 nm (15.6 kK).

Analytical Procedures :

Estimation of copper :

Generally copper was estimated iodometrically after decomposing the complex with  $\text{HNO}_3\text{-H}_2\text{SO}_4$  mixture. But for  $\text{[Cu(pic)(BigH)Cl]}$ ,  $\text{[Cu(o-phen)(BigH)Cl}_2\text{]}$ ,  $\text{[Cu(dipy)(BigH)Cl}_2\text{]}$ ,  $\text{[Cu(dipy)}_2\text{Cl}_2\text{]}$ ,  $\text{[Cu(o-phen)}_2\text{Cl}_2\text{]}$ ,  $\text{[Cu(IDA)(BigH)]}$ ,  $\text{[Cu(dipy)(IDA)]}$  and  $\text{[Cu(o-phen)(IDA)]}$ , the complexes were fused with  $\text{KHSO}_4$  (10-15 times by weight). The cooled mass was dissolved in conc.  $\text{HNO}_3$  containing two drops of conc.  $\text{H}_2\text{SO}_4$  and the whole mass was extracted with water. The solution was next boiled with urea, neutralised with  $\text{NaOH}$  (2N) and then acidified by 1:1 acetic acid. Then  $\text{KI}$  was added and copper was estimated iodometrically.

Estimation of nickel :

The complex was dissolved by  $\text{HNO}_3\text{-H}_2\text{SO}_4$  to dense white fumes. It was then diluted with water, neutralised and nickel(II) precipitated by dimethyl glyoxime as usual.

Estimation of palladium :

Palladium was estimated by igniting the complex and weighing the metallic palladium.

Estimation of cobalt :

The complex was ignited to cobalt oxide which was then treated with  $\text{HCl-H}_2\text{SO}_4$  and finally anhydrous  $\text{CoSO}_4$  was weighed.

Estimation of nitrogen :

Nitrogen was estimated by combustion technique (Duma's method).

Estimation of anions :

Halogens were estimated as silver halides and sulphate as barium sulphate.

Water of hydration :

Water of hydration was determined by loss at 105-110°C for two hours.

Determination of solubilities of copper(II) and nickel(II) complexes :

Solubilities of nickel(II) and copper(II) complexes of biguanide, substituted biguanides and of 1-amidino-0-alkylureas were determined by shaking at room temperature (29-30°C) a known excess of the complex salt in a suitable volume of the developer (10, 20 or 25 ml) for 3 hours. The excess was filtered off by means of gooch no.4, washed with a few drops of ice cold water, dried at 110°C and weighed.

Conductance :

Conductivities in water were measured by Phillips Conductivity Bridge type PR 9500.

Magnetic moments :

The magnetic susceptibility measurements of the complexes at room temperature were made by a Gouy Balance with field strength of about 7500 gauss using G.R. grade  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  as a standard.

Diamagnetic corrections were taken from Selwood<sup>267</sup>. The corrected  $\chi_M$  was converted to  $\mu$  by the well known Curie equation:

$$\mu = 2.84 \sqrt{\chi_M \cdot T}.$$

Absorption spectral measurements :

Absorption spectra of biguanide complexes of copper(II) in water and in aqueous KCl-pyridine mixture were measured at  $5 \times 10^{-3}M$  concentration over the range of 400-800 nm and at  $3 \times 10^{-3}M$  concentration for 1-amidino-O-alkylurea complexes over the range of 400-800 nm in a Hilger and Watts UVISPEK Spectrophotometer using 1 cm cells.

Absorption spectra of the biguanide complexes of nickel(II) in water and in aqueous KCl-pyridine developers were measured at  $5 \times 10^{-3}M$  concentration over the range of 350-600 nm and at  $3 \times 10^{-5}M$  concentration for 1-amidino-O-alkylurea complexes over the same range.

Absorption spectra of the biguanide and 1-amidino-O-alkylurea complexes of palladium(II) in water and in aqueous KCl-pyridine developer were measured at  $5 \times 10^{-4}M$  concentration over the range of 280-400 nm.

Table 3.1. Absorption spectra and structure characterisation of some copper(II) chelates.

Compound	State	Absorption max., $\text{cm}^{-1}$ ( $\epsilon_{\text{molar}}$ for solution)	Suggested stereochemistry and chromophore.	Ref.		
$[\text{Cu}(\text{H-sal DPT})]$	Solid	10, 200 sh; 12500	trigonal bipyramid, $\text{CuN}_3\text{O}_2$	268		
	$\text{CHCl}_3$	12, 350 (213)				
	py	12, 350 (253)				
$[\text{Cu}(\text{H-salMe DPT})]$	Solid	11, 000 sh; 12,270	" "	$\text{CuN}_3\text{O}_2$	268	
$[\text{Cu}(\text{sal})(\text{sal NMe}_2)]$	Nujol Mull	14,600; 16,600 sh	"	"	$\text{CuN}_2\text{O}_3$	262
	$\text{CHCl}_3$	14,100 (274)				
		14,660 (194)				
	py	13,900 (265)				
		15,900 (192) sh				
$[\text{Cu}(\text{sal})(\text{sal NEt}_2)]$	Nujol Mull	13,300; 15,500 sh	"	"	$\text{CuN}_2\text{O}_3$	262
	$\text{CHCl}_3$	13,700 (208)				
		14,800 (190) sh				
	py	13,900 (200)				
		14,800 (190) sh				
$[\text{Cu}(\text{hac})(\text{hac NMe}_2)]$	Nujol Mull	14,300; 16,600	"	"	$\text{CuN}_2\text{O}_3$	262
	$\text{CHCl}_3$	14,300 (206)				
		16,000 (216)				
	py	14,300 (227)				
		16,100 (187) sh				

Table 3.1.(Contd.)

Compound	State	Absorption max., $\text{cm}^{-1}$ ( $\epsilon_{\text{molar}}$ for solution)	Suggested stereochemistry and chromophore.	Ref.
$\left[ \text{Cu}(\text{dien Me}) \text{Cl}_2 \right]^-$	Solid	13, 100	trigonal bipyramid	263
	$\text{CHCl}_3$	12, 700 (259)		
	$\text{C}_2\text{H}_5\text{NO}_2$	12, 500 (236)		
		21, 100 (62)		
$\left[ \text{Cu}(\text{dien Me}) \text{Br}_2 \right]^-$	Solid	13, 000	" "	263
$\left[ \text{Cu}(\text{tren Me}) \text{Br} \right] \text{Br}$	Solid	10, 000	" "	264
		12, 800		
		27, 000 sh		
	$\text{CHCl}_3$	10, 400 (450)		
		13, 300 (209)		
$\left[ \text{Cu}(\text{trenMe}) \text{ClO}_4 \right]^- \text{ClO}_4$	Solid	11, 300; 13,500 sh	" "	264
	$\text{C}_2\text{H}_5\text{NO}_2$	11, 200 (444); 13,800 sh		
$\left[ \text{Cu}(\text{sal-Me})_2 \right]^-$	Solid	11, 000 sh; 13,000	" "	269
$\left[ \text{Cu}(\text{tfac DPT}) \right]^-$	$\text{CH}_3\text{OH}$	12, 422 (245)	square pyramidal	265
		26, 490(512) sh		
		33, 333(15,250)		
		35, 840(11,700) sh		
		42, 020 (10,750)		
$\left[ \text{Cu}(1,2\text{-pn})_2(\text{Su}) \right]^{2+}$	Reflectance	17, 540	" "	$\text{CuN}_5$

Table 3.1.(Contd.)

Compound	State	Absorption max., $\text{cm}^{-1}$ ( $\epsilon_{\text{molar}}$ for solution)	Suggested stereochemistry and chromophore.	Ref.
$[\text{Cu}(\text{o-phen})_2(\text{CN})]^{+}$	Nujol	13, 300	trigonal bipyramidal	266
$[\text{Cu}(\text{BigH})_2]\text{Cl}_2$	Water	19, 230(38.5)	square planar, $\text{CuN}_4$	226
	Water	19, 230-18,870(41)	" " $\text{CuN}_4$	252
$[\text{Cu}(\text{AMUH})_2]\text{Cl}_2$	Water	18, 515(43)	" " $\text{CuN}_4$	244
$[\text{Cu}(\text{AMUH})_2]\text{Ac}_2$	Water	18, 180-18,350	" " $\text{CuN}_4$	244
	$\text{CH}_3\text{OH}$	19, 050-19,160	" " $\text{CuN}_4$	244
	DMSO	19, 800-20,200	" " $\text{CuN}_4$	244
$[\text{Cu}(\text{Bzd})_4]$	Solid	19, 000	" " $\text{CuN}_4$	230
	Acetone	17, 400(71)	distorted octahedral	230
	$\text{CH}_3\text{OH}$	15, 650(69)	" "	230
$[\text{Cu}(\text{en})_2](\text{CNS})_2$	Solid	19, 400	square planar, $\text{CuN}_4$	270
	$\text{CH}_3\text{OH}$	17, 500 (83)	solvation due to solvolysis	270
	Reflectance	19, 080	square planar, $\text{CuN}_4$	271
$[\text{Cu}(\text{en})_2](\text{ClO}_4)_2$	Water	18, 200 (64)	" " $\text{CuN}_4$	229
	$\text{C}_2\text{H}_5\text{OH}$	1850 (63)		229
	Acetone	1850 (63)		229
	$\text{CH}_3\text{NO}_2$	1790 (60)		229
	py	1700 (96)	five or six coordinated species	229
$[\text{Cu}(\text{pa})(\text{pa H})]\text{Cl}$	Reflectance	25840	square planar, $\text{CuN}_4$	272



Table 3.2. Bis(biguanide) copper(II) complexes.

Complex	Preparative Reference	Analysis					
		Metal		Anion		Water of crystallisation	
		Found	Calcd.	Found	Calcd.	Found	Calcd.
$\angle \bar{\text{Cu}}(\text{BigH})_2 \cdot 7\text{Cl}_2 \cdot 2\text{H}_2\text{O}$	221,222	17.0	17.1	19.2	19.2	9.5	9.6
$\angle \bar{\text{Cu}}(\text{Me-BigH})_2 \cdot 7\text{Cl}_2 \cdot 0.5\text{H}_2\text{O}$	221,273,274	17.0	17.0	19.1	19.0	2.6	2.4
$\angle \bar{\text{Cu}}(\text{Et-BigH})_2 \cdot 7\text{Cl}_2 \cdot 2\text{H}_2\text{O}$	221,273,274	14.8	14.8	16.8	16.6	8.7	8.4
$\angle \bar{\text{Cu}}(\text{Pr}^1\text{-BigH})_2 \cdot 7\text{Cl}_2 \cdot \text{H}_2\text{O}$	221	14.4	14.5	14.4	14.3	4.3	4.1
$\angle \bar{\text{Cu}}(\text{Me}_2\text{-BigH})_2 \cdot 7\text{Cl}_2 \cdot 2\text{H}_2\text{O}$	221,274	14.7	14.7	16.0	16.1	10.5	10.2
$\angle \bar{\text{Cu}}(\text{Et}_2\text{-BigH})_2 \cdot 7\text{Cl}_2$	221,274	14.2	14.2	16.0	15.9	-	-
$\angle \bar{\text{Cu}}(\text{Ph-BigH})_2 \cdot 7\text{Cl}_2 \cdot 6\text{H}_2\text{O}$	221,275	10.7	10.6	12.0	11.9	17.9	18.1
$\angle \bar{\text{Cu}} \text{Et}(\text{BigH})_2 \cdot 7\text{Cl}_2 \cdot 0.5\text{H}_2\text{O}$	221,276	17.2	17.2	19.0	19.2	2.6	2.4

Table 3.3. Bis(biguanide) nickel(II)/palladium(II) complexes.

Complex	Preparative Reference	Analysis					
		Metal		Anion		Water of crystallisation	
		Found	Calcd.	Found	Calcd.	Found	Calcd.
$\angle \bar{\text{Ni}}(\text{BigH})_2 \cdot 7\text{Cl}_2 \cdot 2\text{H}_2\text{O}$	221,232	15.8	15.9	19.2	19.3	9.7	9.8
$\angle \bar{\text{Ni}}(\text{Me-BigH})_2 \cdot 7\text{Cl}_2 \cdot 4\text{H}_2\text{O}$	221	13.4	13.5	16.4	16.6	16.6	16.6
$\angle \bar{\text{Ni}}(\text{Et-BigH})_2 \cdot 7\text{Cl}_2 \cdot 0.5\text{H}_2\text{O}$	221	14.6	14.8	17.9	17.9	1.9	2.0
$\angle \bar{\text{Ni}}(\text{Pr}^1\text{-BigH})_2 \cdot 7\text{Cl}_2 \cdot 1.5\text{H}_2\text{O}$	221	13.2	13.3	15.9	16.1	6.3	6.1
$\angle \bar{\text{Ni}}(\text{Me}_2\text{-BigH})_2 \cdot 7\text{Cl}_2 \cdot 0.5\text{H}_2\text{O}$	221	14.7	14.7	17.6	17.8	2.0	2.2
$\angle \bar{\text{Ni}}(\text{Et}_2\text{-BigH})_2 \cdot 7\text{Cl}_2$	221,	13.3	13.3	16.1	16.1	-	-
$\angle \bar{\text{Ni}}(\text{Ph-BigH})_2 \cdot 7\text{Cl}_2 \cdot 0.5\text{H}_2\text{O}$	221,275	11.2	11.1	13.3	13.4	8.6	8.5
$\angle \bar{\text{Ni}} \text{Et}(\text{BigH})_2 \cdot 7 \text{Cl}_2$	221,276	16.3	16.5	19.5	19.9	-	-
$\angle \bar{\text{Pd}}(\text{BigH})_2 \cdot 7\text{Cl}_2 \cdot 2\text{H}_2\text{O}$	221,234	25.8	25.7	17.0	17.2	8.8	8.7
$\angle \bar{\text{Pd}}(\text{Me-BigH})_2 \cdot 7\text{Cl}_2 \cdot 3\text{H}_2\text{O}$	221,277	23.2	23.0	15.3	15.4	11.8	11.7
$\angle \bar{\text{Pd}}(\text{Et-BigH})_2 \cdot 7\text{Cl}_2 \cdot 2\text{H}_2\text{O}$	221,277	22.4	22.5	14.9	15.1	7.9	7.6
$\angle \bar{\text{Pd}}(\text{Ph-BigH})_2 \cdot 7\text{Cl}_2 \cdot 4\text{H}_2\text{O}$	221,277	17.8	17.7	11.7	11.8	11.9	12.0

Table 3.4. Bis(1-amidino-O-alkylurea) copper(II)/nickel(II) complexes.

Complex	Preparative Reference	Analysis					
		Metal		Anion		Water of crystallisation	
		Found	Calcd.	Found	Calcd.	Found	Calcd.
$\angle\bar{\text{Cu}}(\text{AMUM})_2\text{Cl}_2$	223,243,244	17.4	17.3	19.3	19.3	-	-
$\angle\bar{\text{Cu}}(\text{AEUH})_2\text{Cl}_2 \cdot 1.5\text{H}_2\text{O}$	223,243,244	15.1	15.1	16.8	16.8	6.4	6.4
$\angle\bar{\text{Cu}}(\text{AP}^{\text{n}}\text{UH})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$	This study	13.8	13.8	15.4	15.5	7.8	7.8
$\angle\bar{\text{Cu}}(\text{AP}^{\text{i}}\text{UH})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$	223,243,244	13.8	13.8	15.3	15.5	7.7	7.8
$\angle\bar{\text{Cu}}(\text{AB}^{\text{n}}\text{UH})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$	223,243,244	13.0	13.1	14.6	14.6	7.3	7.4
$\angle\bar{\text{Cu}}(\text{AB}^{\text{i}}\text{UH})_2\text{Cl}_2 \cdot 1.5\text{H}_2\text{O}$	223,243,244	13.3	13.3	14.8	14.9	5.5	5.6
$\angle\bar{\text{Cu}}(\text{AA}^{\text{n}}\text{UH})_2\text{Cl}_2 \cdot \text{H}_2\text{O}$	This study	12.8	12.8	14.1	14.3	3.9	3.6
$\angle\bar{\text{Cu}}(\text{AA}^{\text{i}}\text{UH})_2\text{Cl}_2 \cdot \text{H}_2\text{O}$	223,243,244	12.7	12.8	14.2	14.3	3.5	3.6
$\angle\bar{\text{Ni}}(\text{AMUH})_2\text{Cl}_2$	223,243,244	16.2	16.2	19.5	19.6	-	-
$\angle\bar{\text{Ni}}(\text{AEUH})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$	223,243,244	13.8	13.8	16.7	16.7	8.3	8.5
$\angle\bar{\text{Ni}}(\text{AP}^{\text{n}}\text{UH})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$	This study	12.8	12.9	15.6	15.6	7.8	7.9
$\angle\bar{\text{Ni}}(\text{AP}^{\text{i}}\text{UH})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$	223,243,244	12.7	12.9	15.5	15.6	8.1	7.9
$\angle\bar{\text{Ni}}(\text{AB}^{\text{n}}\text{UH})_2\text{Cl}_2 \cdot \text{H}_2\text{O}$	223,243,244	12.5	12.7	15.4	15.3	4.2	3.9
$\angle\bar{\text{Ni}}(\text{AB}^{\text{i}}\text{UH})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$	223,243,244	12.2	12.2	14.8	14.7	7.4	7.5
$\angle\bar{\text{Ni}}(\text{AA}^{\text{n}}\text{UH})_2\text{Cl}_2 \cdot \text{H}_2\text{O}$	This study	12.0	11.9	14.3	14.4	3.5	3.7
$\angle\bar{\text{Ni}}(\text{AA}^{\text{i}}\text{UH})_2\text{Cl}_2 \cdot 1.5\text{H}_2\text{O}$	223,243,244	11.7	11.7	14.1	14.2	5.5	5.4
$\angle\bar{\text{Ni}}(\text{en})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$	278	15.1	15.1	18.2	18.3	10.5	10.4

Table 3.5. Copper(II) mixed chelates and some related copper(II) homo chelates

Complex	Preparative Reference	Analysis						Water of crystallisation	
		Metal		Anion		Nitrogen		Found	Calcd.
		Found	Calcd.	Found	Calcd.	Found	Calcd.		
$\overline{\text{Cu}}(\text{dipy})(\text{IDA}) \cdot 6\text{H}_2\text{O}$	253	13.8	13.8	-	-	8.9	9.1	23.3	23.3
$\overline{\text{Cu}}(\text{o-phen})(\text{IDA}) \cdot 2.5\text{H}_2\text{O}$	253	14.9	15.1	-	-	10.3	10.0	10.4	10.7
$\overline{\text{Cu}}(\text{BigH})(\text{IDA}) \cdot 1.5\text{H}_2\text{O}$	253	19.5	19.7	-	-	25.8	26.1	8.1	8.4
$\overline{\text{Cu}}(\text{gly})(\text{BigH}) \cdot 1.5\text{H}_2\text{O}$	221,250	21.1	21.1	12.0	11.8	-	-	8.6	9.0
$\overline{\text{Cu}}(\text{gly})(\text{Me-BigH}) \cdot 1.0.5\text{H}_2\text{O}$	221,250	21.4	21.4	12.1	12.0	-	-	2.8	3.0
$\overline{\text{Cu}}(\text{gly})(\text{Et-BigH}) \cdot 1.0.5\text{H}_2\text{O}$	221,250	20.4	20.4	11.4	11.4	-	-	2.7	2.8
$\overline{\text{Cu}}(\alpha\text{-alan})(\text{BigH}) \cdot 1.3\text{H}_2\text{O}$	221,250	18.5	18.5	10.3	10.3	-	-	16.0	15.9
$\overline{\text{Cu}}(\alpha\text{-alan})(\text{Me-BigH}) \cdot \text{Cl}$	221,250	22.1	22.1	11.0	11.1	-	-	-	-
$\overline{\text{Cu}}(\alpha\text{-alan})(\text{Et-BigH}) \cdot 1.2\text{H}_2\text{O}$	221,250	18.0	18.0	10.1	10.1	-	-	-	-
$\overline{\text{Cu}}(\text{gly})(\text{o-phen}) \cdot 1.3\text{H}_2\text{O}$	252	15.5	15.5	8.6	8.7	-	-	13.3	13.2
$\overline{\text{Cu}}(\text{gly})(\text{dipy}) \cdot 1.1.5\text{H}_2\text{O}$	252	17.7	17.8	9.8	9.7	-	-	7.8	7.6

Table 3.5.(Contd.)

Complex	Preparative Reference	Analysis						Water of crystallisation	
		Metal		Anion		Nitrogen		Found	Calcd.
		Found	Calcd.	Found	Calcd.	Found	Calcd.		
$\overline{\text{Cu}}(\text{dipy})(\text{BigH})\overline{\text{Cl}}_2 \cdot 1.5\text{H}_2\text{O}$	251	15.2	15.2	16.8	16.9	-	-	6.8	6.5
$\overline{\text{Cu}}(\text{dipy})(\text{Me-BigH})\overline{\text{Cl}}_2 \cdot 2\text{H}_2\text{O}$	251	14.4	14.4	16.0	16.1	-	-	8.3	8.2
$\overline{\text{Cu}}(\text{dipy})(\text{Et-BigH})\overline{\text{Cl}}_2 \cdot 3\text{H}_2\text{O}$	251	13.3	13.4	15.0	15.0	-	-	11.5	11.4
$\overline{\text{Cu}}(\text{o-phen})(\text{BigH})\overline{\text{Cl}}_2 \cdot 2\text{H}_2\text{O}$	251	14.0	14.1	15.9	15.8	-	-	8.2	8.0
$\overline{\text{Cu}}(\text{pic})(\text{BigH})\overline{\text{Cl}}$	This study	19.7	19.7	10.9	11.0	26.2	26.1	-	-
$\overline{\text{Cu}}(\text{gly})_2\overline{\text{O}} \cdot 0.5\text{H}_2\text{O}$	279	28.7	28.7	-	-	12.6	12.7	4.1	4.0
$\overline{\text{Cu}}(\alpha\text{-alan})_2\overline{\text{H}}_2\text{O}$	279	25.0	25.0	-	-	11.0	11.0	7.0	7.1
$\overline{\text{Cu}}(\text{dipy})_2\overline{\text{Cl}}_2 \cdot 1.5\text{H}_2\text{O}$	280	-	-	14.9	15.0	11.8	11.8	5.6	5.7
$\overline{\text{Cu}}(\text{o-phen})_2\overline{\text{Cl}}_2 \cdot 2\text{H}_2\text{O}$	280	-	-	13.4	13.3	10.3	10.5	6.7	6.9
$\overline{\text{Cu}}(\text{en})_2\overline{\text{NO}}_3)_2$	281	20.6	20.7	-	-	27.3	27.3	-	-

Table 3.6. Cobalt(III) complexes.

Complex	Preparative Reference	Analysis						Water of crystallisation	
		Metal		Anion		Nitrogen		Found	Calcd.
		Found	Calcd.	Found	Calcd.	Found	Calcd.		
$\angle \bar{\text{Co}}(\text{BigH})_3 \bar{\text{Cl}}_3$	221,245	12.8	12.7	22.7	22.8	-	-	-	-
$\angle \bar{\text{Co}}(\text{BigH})_3 \bar{\text{Cl}}_2 (\text{SO}_4)_3$	221,245	11.8	11.7	28.8	28.6	-	-	-	-
$\angle \bar{\text{Co}}(\text{NH}_3)_6 \bar{\text{Cl}}_3$	282	21.8	22.0	39.7	39.8	-	-	-	-
$\angle \bar{\text{Co}}(\text{en})_3 \bar{\text{Br}}_3$	283	12.0	12.3	49.9	50.1	-	-	-	-
$\angle \bar{\text{Co}}(\text{Ph-BigH})_3 \bar{\text{Cl}}_3 \cdot 2.5\text{H}_2\text{O}$	221,284	8.1	7.9	14.3	14.4	-	-	4.9	6.1
$\angle \bar{\text{Co}}(\text{dipy})(\text{BigH})_2 \bar{\text{Cl}}_3 \cdot 3\text{H}_2\text{O}$	247	10.1	10.2	18.3	18.4	-	-	9.2	9.3
$\angle \bar{\text{Co}}(\text{o-phen})(\text{BigH})_2 \bar{\text{Cl}}_3$	247	10.7	10.8	19.2	19.4	-	-	-	-
$\angle \bar{\text{Co}}(\alpha\text{-alan})(\text{BigH})_2 \bar{\text{Cl}}_2 \cdot 2\text{H}_2\text{O}$	249	12.7	12.9	15.4	15.6	33.6	33.8	8.0	7.9
$\angle \bar{\text{Co}}(\Delta\text{-alan})(\text{BigH})_2 \bar{\text{I}}_2$	249	9.5	9.8	42.3	42.1	25.1	25.6	-	-
$\angle \bar{\text{Co}}(\text{leuc})(\text{BigH})_2 \bar{\text{Cl}}_2 \cdot 3\text{H}_2\text{O}$	249	11.3	11.4	13.7	13.8	29.6	29.8	10.0	10.5
$\angle \bar{\text{Co}}(\text{val})(\text{BigH})_2 \bar{\text{Cl}}_2 \cdot 4.5\text{H}_2\text{O}$	249	11.1	11.1	13.3	13.4	28.9	29.1	15.0	15.3

Table 3.6.(Contd.)

Complex	Preparative Reference	Analysis						Water of crystallisation	
		Metal		Anion		Nitrogen		Found	Calcd.
		Found	Calcd.	Found	Calcd.	Found	Calcd.		
$\overline{\text{Co}}(\text{hist})(\text{BigH})_2\overline{\text{I}}_2 \cdot \text{H}_2\text{O}$	249	8.7	8.6	36.7	36.9	26.6	26.5	2.8	2.7
$\overline{\text{Co}}(\text{meth})(\text{BigH})_2\overline{\text{I}}_2$	249	9.0	8.7	36.9	37.3	23.0	22.6	-	-
$\overline{\text{Co}}(\text{pic})(\text{BigH})_2\overline{\text{I}}_2 \cdot 1.5\text{H}_2\text{O}$	248	-	-	-	-	23.1	23.2	3.9	4.0
$\overline{\text{Co}}(\text{lut})(\text{BigH})_2\overline{\text{Cl}} \cdot 3\text{H}_2\text{O}$	248	11.4	11.5	6.7	6.8	29.9	30.0	10.4	10.5
$\overline{\text{Co}}(\text{IDA})(\text{BigH})_2\overline{\text{Br}} \cdot \text{H}_2\text{O}$	248	12.2	12.1	16.3	16.4	31.5	31.6	3.5	3.6
$\overline{\text{Co}}(\text{en})_2 \text{CO}_3\overline{\text{Cl}}$	285	21.6	21.5	12.9	12.9	-	-	-	-
$\overline{\text{Co}}(\text{en})_2 \text{CO}_3\overline{\text{NO}}_3$	285	19.6	19.6	-	-	23.3	23.3	-	-
$\overline{\text{Co}}(\text{NH}_3)_3(\text{NO}_2)_3\overline{\text{}}$	286	23.9	23.8	-	-	33.8	33.9	-	-
$\text{K}\overline{\text{Co}}(\text{gly})_2(\text{NO}_2)_2\overline{\text{}}$	287	17.3	17.4	-	-	16.4	16.6	-	-
$\text{NH}_4\overline{\text{Co}}(\text{NH}_3)_2(\text{NO}_2)_4\overline{\text{}}$	288	19.9	20.0	-	-	33.1	33.2	-	-
$\text{Na}_3\overline{\text{Co}}(\text{NO}_2)_6\overline{\text{}}$	289	14.4	14.6	-	-	20.7	20.8	-	-
$\text{K}_3\overline{\text{Co}}(\text{Ox})_3\overline{\text{}}$	290	13.4	13.4	-	-	-	-	-	-

## B. Methods.

### (a) Paper Chromatography :

Paper chromatography was usually carried out on Whatman No.1 paper strips 3 cm x 52 cm using ascending technique. But for comparative studies of more than one compound the paper was 5 cm x 52 cm. The sample solution was applied at a point 8 cm from the end with the aid of a capillary and the developer was allowed to travel 28-30 cm from the point of application. The time required was about 3 hours unless otherwise specified. The total volume of the developer was about 100 ml. The chromatographic chamber (a talljar of 10 cm x 62 cm) was saturated with the vapour of the developer for at least one day. The development was carried out at room temperature (27 - 30°C).

For the detection of copper(II) and nickel(II) complexes (both for paper and TLC) rubeanic acid in ethanol was satisfactory; for palladium(II) complexes acidified (HCl) solution of rubeanic acid was found quite sensitive. Generally cobalt(III) complexes are easily visualised by aqueous solution of  $\text{Na}_2\text{S}$ . But for few of our cobalt(III) complexes e.g.  $[\text{Co}(\text{BigH})_3]^{3+}$ ,  $[\text{Co}(\text{dipy})(\text{BigH})_2]^{3+}$ ,  $[\text{Co}(\text{o-phen})(\text{BigH})_2]^{3+}$ ,  $[\text{Co}(\text{hist})(\text{BigH})_2]^{3+}$ , the filter paper was first sprayed with acidified (HCl) solution of rubeanic acid, dried and finally sprayed with aqueous solution of  $\text{Na}_2\text{S}$  when brown to black spots appeared.  $R_f$  values were measured at the centre of the distance between the front and end of the spot as suggested by Lacourt et al<sup>291</sup>. These  $R_f$  values were reproducible to within  $\pm 0.02 R_f$  units.



(b) Thin Layer Chromatography (TLC) :

Merck's silica gel H was chosen as an adsorbent. This adsorbent was slurried with distilled water (two parts water to one part adsorbent) and spread on the glass plates (5 cm x 20.5 cm or 8 cm x 20.5 cm). The thickness of the plates was always maintained around 0.25 mm with the help of 'Moving spreader' apparatus. The plates were dried in air for 20 minutes and heated at 105-110°C for one hour. Then the plates were stored in a desiccator as prescribed by Browning<sup>292</sup> and Stahl<sup>293</sup>.

The chromatographic chambers (11 cm x 25 cm) were saturated with the developers ( 400 ml) for at least two days. The sample was applied at a point 4 cm from one end. The developer was then allowed to travel 13-14 cm from the point of application. Running time for the chromatogram was about 30 minutes.  $R_f$  values were reproducible to within  $\pm 0.02 R_f$  units.