

APPENDIX I
PUBLISHED PAPERS

Research Publications :

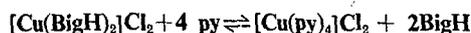
1. Chromatographic Studies on Metal Complexes. Part I.
Paper Chromatography of Square Planar bis(biguanide)
Copper(II), Nickel(II) and Palladium(II) Complexes.
R.L.Dutta and R.K.Ray, J.Indian Chem.Soc.,1974,51,187.
2. Chromatographic Studies on Metal Complexes. Part II.
Paper Chromatography of Copper(II) Mixed Chelates.
R.L.Dutta and R.K.Ray, J.Indian Chem.Soc.,1975,52,387.
3. Chromatographic Studies on Metal Complexes. Part III.
Paper Chromatography of Square Planar bis(1-amidino-
O-alkylurea) Copper(II) and Nickel(II) Complexes.
R.L.Dutta and R.K.Ray, J.Indian Chem.Soc.,1975,52,579.
4. Chromatographic Studies on Metal Complexes. Part IV.
Palladium(II) Complexes of 1-amidino-O-alkylureas.
R.L.Dutta and R.K.Ray, J.Indian Chem.Soc.,
(accepted for publication.)

Chromatographic Studies on Metal Complexes Part I Paper Chromatography of Square planar bis(biguanide) Complexes of Copper (II), Nickel (II) and Palladium (II)

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A paper chromatographic study of square planar bis(biguanide) complexes of copper(II), nickel(II) and palladium(II) in aqueous pyridine developer has been made. R_f values decrease in the order: Ni(II) > Cu(II) > Pd(II). R_f values increase with increasing alkyl substitution in the biguanide moiety of a particular metal complex. Phenyl substitution lowers the R_f . Substantial amount of pyridine in the developer results in two spots with bis(biguanide) copper(II). The following equilibrium is suggested:



MOST studies on paper chromatography of inorganic cations have been directed with a view to their identification via characteristic R_f value in a chosen developer. Paper chromatographic studies on metal complexes have mainly veered around inert cobalt (III)¹. Little work on the complexes of other transition metals has appeared in the literature. The purpose of this study of square planar bis(biguanide) metal(II) complexes has been multifold: (1) to determine a suitable developer such that the complexes are chromatographed as genuine bis(biguanide) complexes; (2) to study the effect, if any, of substitution in the biguanide moiety on the R_f values of the complexes and (3) to determine the influence of the transition metals on R_f .

Methods and Materials:

The complexes have been obtained by following published procedures². Their purity was checked by analysis and spectral measurement.

Experimental Conditions:

For the purpose of putting spots most of the complexes were dissolved in water at room temperature or in warm water. In a few cases (e.g. those of copper dimethyl, diethyl and phenylbiguanide) complexes were dissolved in ethanol because of greater solubility in this solvent. The following developers were selected after a number of trials:

Developer I: 100ml of 0.5M aqueous KCl + 5ml pyridine

Developer II: 100ml of 1.0M aqueous KCl + 5ml pyridine

Developer III: 70ml of 0.5M aqueous KCl
30ml 1 : 1 pyridine

The total volume of the developer was about 100ml. The chromatographic chamber was saturated with the vapour of the developer for at least one day. Chromatography was carried out on Whatman No. 1 paper strips (3cm × 52 cm) using ascending technique. The sample solution was applied at a point 8cm from the end and the developer was allowed to travel 28-30cm from the point of application of the spot. The time required was about 3 hours.

For the detection of copper and nickel complexes rubeanic acid in ethanol was satisfactory. Palladium complexes were detected with acidified (HCl) solution of rubeanic acid. Bis(biguanide)copper(II) complex on spraying with rubeanic acid gave an oval shaped spot, the lower portion of the spot having a dominant brown colour while the upper part had the usual dirty green colour of copper rubeanate. But most of the substituted biguanide copper(II) complexes gave only a dirty green coloured spot on spraying with rubeanic acid. Nickel complexes had the blue to blue violet colour of nickel rubeanate and palladium complexes a yellow colour of palladium rubeanate. The brown shade in the spot of bis(biguanide)copper(II) chloride was not subjected to any further investigation. R_f values were measured with respect to the centre of the distance between the front and the end of the spot. These R_f values were reproducible to within $\pm 0.02 R_f$ units.

Results and Discussion :

Developer I was quite satisfactory for identification and separation of copper(II) and palladium(II) bis(biguanide) complexes from one another. This developer was also suitable for separation and identification of bis(biguanide)copper(II) from bis (substituted biguanide)copper(II). In this developer both copper(II) and palladium(II) complexes provide well defined spots, those of copper(II) being ~ 2.5 — 3.0 cm in length and those of palladium(II) ~ 1.0 cm. Bis(phenylbiguanide)palladium(II)chloride alone gives large tailing (~ 5 cm). Unfortunately this developer provided a big sized (10-12cm) spot for bis(biguanide)nickel(II) complexes and was therefore not considered a suitable choice for these nickel(II) complexes. Suitable sized spots (~ 3 cm) of bis(biguanide)nickel(II) and bis(substituted biguanide)nickel(II) complexes were obtained using developer II which also allowed distinction between nickel(II) complexes themselves. But neither developer I nor developer II was found suitable for distinguishing bis(biguanide)palladium(II) and bis(substituted biguanide)palladium(II) complexes from one another. To achieve this distinction developer (III) was found suitable.

Yoneda¹ from a study of cobalt (III) complexes concluded that the cationic complexes are held strongly on the negatively charged cellulose anion of the filter paper. Thus in pure water as developer positively charged complexes either did not travel at all or if they travelled they diffused considerably along the filter paper. With distilled water alone most of our complexes either did not travel at all or diffused to a long distance (Fig. 1). Remembering that metal biguanide complexes are stable to dis-

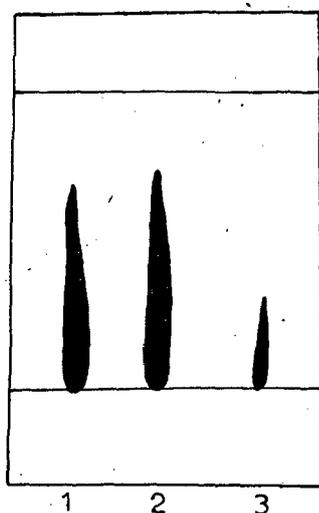


Fig. 1. Chromatograms in 100 ml distilled water as developer

- (1) $[\text{Ni}(\text{BigH})_2]\text{Cl}_2$;
- (2) $[\text{Cu}(\text{BigH})_2]\text{Cl}_2$;
- (3) $[\text{Pd}(\text{BigH})_2]\text{Cl}_2$.

sociation only at $\text{pH} \sim 7.0$, we tried several aqueous electrolytes as developers so that the cations of the electrolyte may quench the undesirable effect of the cellulose anion. Satisfactory spots were obtained with two sets of developers :

- A 0.5M (or 1M) aqueous ammonium acetate
- B. 0.5M (or 1M) aqueous KCl containing pyridine.

The first of these developers (A), although gave a $\text{pH} \sim 6.5$ to 6.8 where metal biguanides do not dissociate appreciably, were abandoned since spectrophotometric studies revealed that for all three copper(II) nickel(II) and palladium(II) complexes there were substantial modification of the electronic spectra. These developers therefore do not give R_f values of the genuine complexes. The developers of category (B) provided the same electronic spectra of the complexes as is obtained in aqueous solution alone. Thus in 100 ml 0.5 M (or 1M) KCl containing 5ml pyridine we have the genuine chromatograms of our complexes.

Effect of KCl/pyridine : Variation of KCl concentration in aqueous pyridine reveals that R_f values of all complexes increase with increasing KCl concentration (Table 1). It is to be noted that neither KCl nor pyridine alone can give good spots (Fig. 2

TABLE 1— R_f VALUES OF $[\text{M}(\text{BigH})_2]\text{Cl}_2$ ($\text{M}=\text{Cu}(\text{II}), \text{Ni}(\text{II}), \text{Pd}(\text{II})$) WITH DIFFERENT DEVELOPERS

Complex	Developer I	Developer II
$[\text{Ni}(\text{BigH})_2]\text{Cl}_2$	0.64	0.78
$[\text{Cu}(\text{BigH})_2]\text{Cl}_2$	0.46	0.53
$[\text{Pd}(\text{BigH})_2]\text{Cl}_2$	0.10	0.23

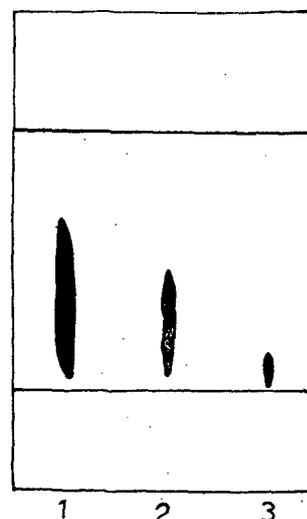


Fig. 2 Chromatograms in 100ml 1M aqueous KCl as developer (1), (2) and (3) are as in Fig. 1.

and 3) but a suitable combination does (Fig. 4). Pyridine substantially increases the solubility of the complexes.

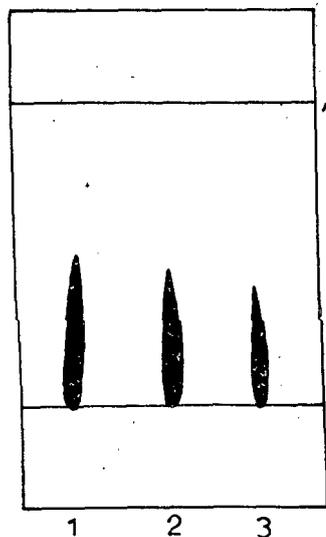


Fig. 3. Chromatograms in 100ml 5% pyridine in water as developer. (1), (2) and (3) are as in Fig. 1.

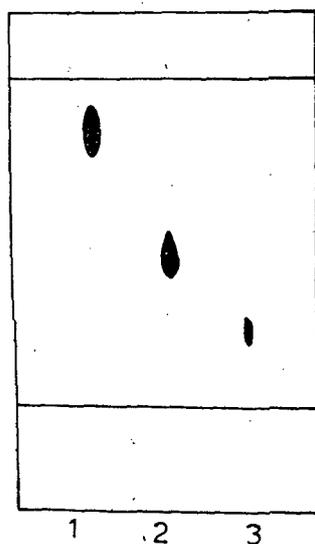


Fig. 4. Chromatograms in 100ml 1M aqueous KCl+5ml pyridine as developer. (1), (2) and (3) are as in Fig. 1.

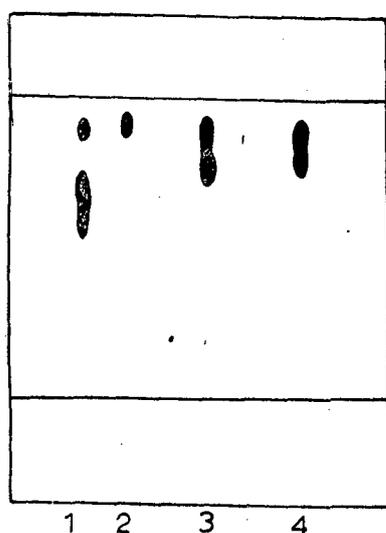
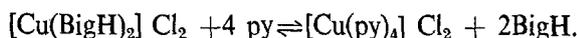


Fig. 5. Chromatograms in 70ml 0.5M aqueous KCl+30ml 1:1 pyridine. (1) $[Cu(BigH)_2]Cl_2$ (2) $CuCl_2$ (3) $[Cu(MeBigH)_2]Cl_2$ (4) $[Cu(EtBigH)_2]Cl_2$.

Interestingly on raising the pyridine concentration and lowering the KCl concentration (developer III) bis(biguanide)copper(II) complex betrayed two distinct spots (Fig. 5), the one with higher R_f was less intense than the other with lower R_f . Furthermore the spot with higher R_f coincided with the spot of copper(II) chloride in the same developer and that with lower R_f had the characteristic shape of bis(biguanide) copper(II) in the same developer. An

explanation possibly lies in the assumption of the following equilibrium :



The low intensity of the tetrapyridinocopper(II) spot would point to the fact that the equilibrium is still favoured towards bis(biguanide)copper(II). With bis(alkylsubstitutedbiguanide)copper(II) distinct separation into two spots could not be achieved possibly because of the higher R_f values of the bis(alkylsubstituted biguanide) compared to that of the bis(biguanide)copper(II). This would lead to a smaller gap between the spots of tetrapyridine copper(II) and bis(alkylsubstituted biguanide) copper(II). But with developer III, nickel(II) complexes did not betray two distinct spots, although the size of the spot was substantially large (~9 cm). Bis(biguanide) palladium(II), however, exhibited only one sharp spot which is an evidence towards preponderance of only one species.

Effect of size of the complexes on R_f values : The increasing R_f values : $Pd < Cu < Ni$ corresponds to the decreasing size and weight of the complexes $Pd > Cu > Ni$ (Table 1 and Fig. 4).

Effect of substitution in biguanide moiety on R_f values :

On increasing alkyl substitution on N^1 atom of biguanide the R_f values of the corresponding copper(II), nickel(II) and palladium(II) bis (biguanide) complexes also increase. But phenyl substitution lowers the R_f (Table 2). Since biguanide and alkyl

TABLE 2— R_f VALUES OF $[M(BigH)_2]Cl_2$ and $[M(SUBSTITUTED BigH)_2]Cl_2$ WITH DIFFERENT DEVELOPERS

Complex	Developer II	Developer I	Developer III
	M=Ni(II)	M=Cu(II)	M=Pd(II)
$[M(BigH)_2]Cl_2$	0.78	0.46	0.40
$[M(Me BigH)_2]Cl_2$	0.83	0.52	0.51
$[M(Et BigH)_2]Cl_2$	0.86	0.64	0.58
$[M(Pr^1 BigH)_2]Cl_2$	0.88	0.68	—
$[M(Me_2 BigH)_2]Cl_2$	0.90	0.72	—
$[M(Et_2 BigH)_2]Cl_2$	0.92	0.78	—
$[M(Ph BigH)_2]Cl_2$	0.76	0.44	0.33

BigH=biguanide ; MeBigH=methyl biguanide ; Et BigH=ethyl biguanide ; Pr^1 BigH=isopropyl biguanide ; Me_2 BigH=dimethyl biguanide ; Et_2 BigH=diethyl biguanide ; Ph BigH=phenylbiguanide.

biguanide have more or less similar basic character it is a reasonable guess that the attractive influence of the bipositive cations on the cellulose anion will be quite close. However, substitution of the hydrogen atom attached to the N¹ atom of the biguanide by hydrophobic groups would considerably reduce the chances of forming hydrogen bonded species with cellulose anions. This is expected to lead to a higher R_f with increasing substitution. Had' solubility alone been responsible for differences in R_f values we would have observed a reverse order with increasing alkyl substitution. Increase of R_f values from biguanide to methyl biguanide and then to other alkyl biguanide is also likely to be connected with inductive influence of the electron releasing alkyl groups whereby the overall charge on the com-

plex cation may be diminished to some extent. This lowering of charge will enhance the R_f values. On the contrary electron withdrawing phenyl substitution will lead to a lower R_f.

This is a pleasure to acknowledge our indebtedness to the C.S.I.R. for financial assistance to one of us (R.K.R.). We thank Dr. S. Ghosh Majumdar and Dr. S. Thakur for their kind advice and suggestions during the course of the work.

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1. H. YONEDA, *Bull. Chem. Soc., Japan*, 1967, **40**, 2442.
2. P. Ray, *Chem. Revs.*, 1961, **61**, 313.

Chromatographic Studies on Metal Complexes. Part II. Paper Chromatographic Studies on Copper(II) Mixed Chelates**

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A paper chromatographic study of fifteen copper(II) mixed chelates in aqueous pyridine developer has been made. $[\text{Cu}(\text{gly})(\text{BigH})]\text{Cl}$, $[\text{Cu}(\alpha\text{-alan})(\text{BigH})]\text{Cl}$ etc. give two spots in all the developers studied. An equilibrium of the following type is suggested:



$[\text{Cu}(\text{gly})(o\text{-phen})]\text{Cl}$ also shows similar behaviour. Such disproportionation reaction is less favoured in $[\text{Cu}(\text{gly})(\text{dipy})]\text{Cl}$. $[\text{Cu}(o\text{-phen})(\text{BigH})]\text{Cl}_2$ and $[\text{Cu}(\text{dipy})(\text{BigH})]\text{Cl}_2$ provide single spot on proper choice of the developer.

MIXED ligand complexes are of considerable current interest. In this paper we report the results of our studies on paper chromatographic behaviour of a number of copper(II) mixed chelates (Table 1).

Methods and Materials

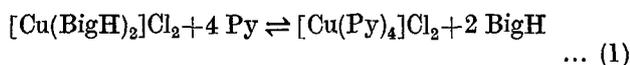
The mixed chelates were obtained by following published procedures¹⁻⁴. Their purity was checked by elemental analysis and spectral measurements. Ascending paper chromatography was adopted. Experimental techniques have been described elsewhere⁵. The following developers were tried:

Developer I :	Distilled water (100 ml)
„ II :	100 ml 1(M) KCl
„ III :	100 ml 0.5(M) KCl + 5 ml Pyridine
„ IV :	100 ml 1(M) KCl + 5 ml Pyridine
„ V :	70 ml 0.5(M) KCl + 30 ml (1 : 1) Pyridine.

R_f values were reproducible to within $\pm 0.02 R_f$ units.

Results and Discussion

We have reported earlier⁵ that with higher concentration of pyridine and low concentration of KCl (as in developer V), the homochelate $[\text{Cu}(\text{BigH})_2]\text{Cl}_2$ provided two spots, which was traced to be due to an equilibrium of the type:



In view of the above results it appeared likely that mixed chelates will provide interesting solvent dependent chromatographic behaviour. A fairly good number of copper(II) mixed chelates (Table 1) were selected for this study. The mixed chelates were repeatedly crystallised. They all provided good analytical values and looked homogeneous single species under the microscope. Their spectra also conformed to published absorption maxima and molar extinction coefficients.

TABLE 1— R_f VALUES OF COPPER(II) MIXED CHELATES WITH DEVELOPER IV

Charge	Complex	R_f
0	$[\text{Cu}(\text{dipy})(\text{IDA})]$	0.87
	$[\text{Cu}(o\text{-phen})(\text{IDA})]$	0.80
	$[\text{Cu}(\text{BigH})(\text{IDA})]$	0.70
+1	$[\text{Cu}(\text{gly})(\text{BigH})]\text{Cl}$	0.53, 0.93
	$[\text{Cu}(\text{gly})(\text{Me-BigH})]\text{Cl}$	0.60, 0.93
	$[\text{Cu}(\text{gly})(\text{Et-BigH})]\text{Cl}$	0.66, 0.93
	$[\text{Cu}(\alpha\text{-alan})(\text{BigH})]\text{Cl}$	0.53, 0.94
	$[\text{Cu}(\alpha\text{-alan})(\text{Me-BigH})]\text{Cl}$	0.60, 0.94
	$[\text{Cu}(\alpha\text{-alan})(\text{Et-BigH})]\text{Cl}$	0.66, 0.94
	$[\text{Cu}(\text{gly})(o\text{-phen})]\text{Cl}$	0.80, 0.91
	$[\text{Cu}(\text{gly})(\text{dipy})]\text{Cl}$	0.80
+2	$[\text{Cu}(\text{dipy})(\text{BigH})]\text{Cl}_2$	0.74
	$[\text{Cu}(\text{dipy})(\text{Me-BigH})]\text{Cl}_2$	0.77
	$[\text{Cu}(\text{dipy})(\text{Et-BigH})]\text{Cl}_2$	0.81
	$[\text{Cu}(o\text{-phen})(\text{BigH})]\text{Cl}_2$	0.71

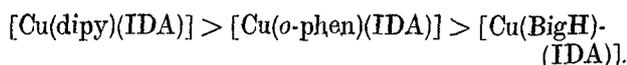
Under similar condition R_f values of the homochelates are: $[\text{Cu}(\text{gly})_2] = 0.93$; $[\text{Cu}(\alpha\text{-alan})_2] = 0.94$; $[\text{Cu}(\text{BigH})_2]\text{Cl}_2 = 0.53$; $[\text{Cu}(\text{Me-BigH})_2]\text{Cl}_2 = 0.60$; $[\text{Cu}(\text{Et-BigH})_2]\text{Cl}_2 = 0.66$; $[\text{Cu}(\text{dipy})_2]\text{Cl}_2 = 0.91$; $[\text{Cu}(o\text{-phen})_2]\text{Cl}_2 = 0.80$; gly H = glycine; $\alpha\text{-alanH}$ = α -alanine; BigH = bigunide; Me-BigH = methyl biguanide; Et-BigH = ethyl biguanide; dipy = dipyriddy; o-phen = orthophenanthroline; IDA_2 = iminodiacetic acid.

** Paper presented at the Convention of Chemists held in Calcutta, December 24-30, 1973.

Developer I is not found suitable. The mixed complexes, whether charged or uncharged, either do not move at all from their point of application or if they move they diffuse to a long distance along the filter paper. This is not surprising for cationic complexes as they are known to be strongly held on the negatively charged cellulose anion of the filter paper⁶. With developer II, although the complexes move from their point of application, the spots are too large. With this developer [Cu(gly)(BigH)]Cl, [Cu(gly)(Me-BigH)]Cl, [Cu(gly)(Et-BigH)]Cl, [Cu(α -alan)(BigH)]Cl, [Cu(α -alan)(Me-BigH)]Cl, [Cu(α -alan)(Et-BigH)]Cl, [Cu(gly)(*o*-phen)]Cl, [Cu(dipy)(BigH)]Cl₂, [Cu(dipy)(Me-BigH)]Cl₂, [Cu(dipy)(Et-BigH)]Cl₂, always give two spots instead of one. [Cu(gly)(dipy)]Cl alone provides single spot in this developer II. Best results are obtained with developer IV, the R_f values being given in the Table 1.

Mixed chelates containing iminodiacetate group (IDA) :

All the three complexes are neutral and provide single spots in developer IV. Their R_f values have the order :

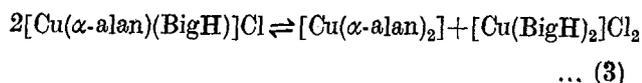
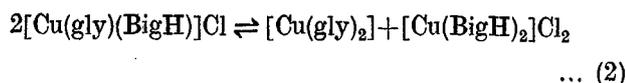


This order is also the order of increasing solubility of the complexes in aqueous KCl—pyridine developer. The mixed chelates seem to possess non-electrolytic nature rather than the electrolytic structure e.g., [Cu(dipy)₂][Cu(IDA)₂]. etc. The electrolytic structure would admit of two spots.

Glycinato mono(biguanide) copper(II) and α -alaninato mono(biguanide) copper(II) and related complexes :

Das Sarma and Ray noted³ that on several crystallisations of these compounds the chemical analysis remained unaffected. We also observed no change in the crystalline behaviour (under the microscope) or in the analysis on several fractional crystallisations. Yet their chromatograms in developer IV provide two spots with very different R_f values. Interestingly the oval shaped spot with lower R_f corresponds to the spot of bis(biguanide) copper(II) and the upper spot with higher R_f is identical with that of bis(amino-acidato) copper(II) under similar conditions (Fig. 1).

These observations point to the following disproportionation reactions :



Whichever developer is chosen, these mixed chelates give, consistently, two spots. That the presence of pyridine in the developer is not responsible for the appearance of two spots was verified by the fact

that even distilled water (as in developer I) and aqueous KCl (as in developer II) could separate the mixed chelates into two component homochelates (Fig. 2 and Fig. 3).

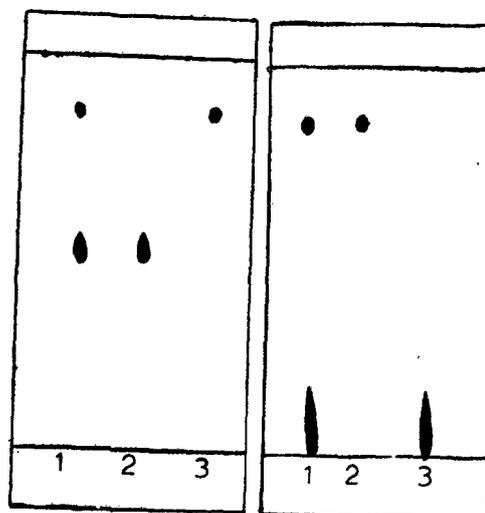


Fig. 1.

Fig. 2.

Fig. 1. Chromatograms in 100 ml 1(M) KCl+5 ml Pyridine as developer (Developer IV).

- (1) [Cu(gly)(BigH)]Cl; (2) [Cu(BigH)₂]Cl₂;
- (3) [Cu(gly)₂].

Fig. 2. Chromatograms in 100 ml distilled water as developer (Developer I)

- (1) [Cu(gly)(BigH)]Cl; (2) [Cu(gly)₂]; (3) [Cu(BigH)₂]Cl₂

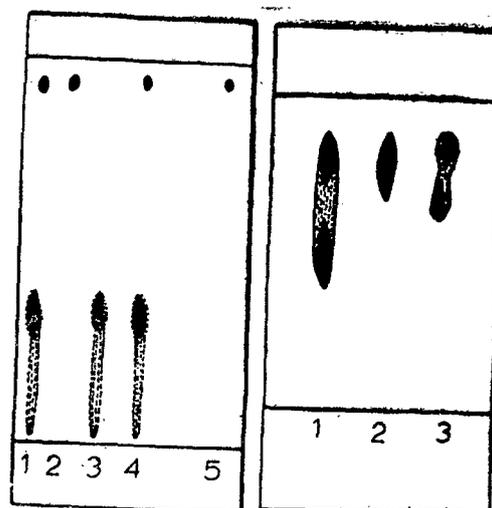


Fig. 3.

Fig. 4.

Fig. 3. Chromatograms in 100 ml 1(M) aqueous KCl as developer (Developer II)

- (1) [Cu(gly)(BigH)]Cl; (2) [Cu(gly)₂];
- (3) [Cu(BigH)₂]Cl₂; (4) [Cu(α -alan)(BigH)]Cl;
- (5) [Cu(α -alan)₂].

Fig. 4. Chromatograms of [Cu(*o*-phen)(BigH)]Cl₂ in different developers.

- (1) 100 ml 0.5(M) KCl+5 ml Pyridine (Developer III).
- (2) 100 ml 1(M) KCl+5 ml Pyridine (Developer IV).
- (3) 70 ml 0.5(M) KCl+30 ml (1 : 1) Pyridine. (Developer V).

In our earlier studies⁵ of $[\text{Cu}(\text{BigH})_2]\text{Cl}_2$ in developer V we had reported chromatographic evidence in favour of equilibrium(1). One would therefore expect three spots of $[\text{Cu}(\text{gly})(\text{BigH})]\text{Cl}$ in developer V, resulting from a secondary equilibrium of $[\text{Cu}(\text{BigH})_2]\text{Cl}_2$ with large excess of pyridine present in developer(V) giving another species $[\text{Cu}(\text{Py})_4]\text{Cl}_2$ according to equilibrium (1). But we have obtained no more than two spots in developer (V). This is readily explained when we consider that $[\text{Cu}(\text{gly})_2]$ and $[\text{Cu}(\text{Py})_4]\text{Cl}_2$ show almost the same R_f in this developer ($[\text{Cu}(\text{gly})_2] = 0.85$; $[\text{Cu}(\text{Py})_4]\text{Cl}_2 = 0.86$).

Glycinato mono(dipyridyl) copper(II) and glycinato mono(o-phenanthroline) copper(II) :

$[\text{Cu}(\text{gly})(\text{dipy})]\text{Cl}$ provides, in developer IV, single spot with $R_f = 0.80$ while $[\text{Cu}(\text{gly})(o\text{-phen})]\text{Cl}$ gives two spots with $R_f = 0.80$ and 0.91. The upper spot with higher R_f is of low intensity and its R_f is comparable to that of $[\text{Cu}(\text{gly})_2]$. The R_f value of $[\text{Cu}(o\text{-phen})_2]\text{Cl}_2$ is also around 0.80. So the following disproportionation reaction is suggested :



Similar disproportionation of $[\text{Cu}(\text{gly})(\text{dipy})]\text{Cl}$ into two homochelates is less favoured since we get one spot with $R_f = 0.80$ which is different from that of either $[\text{Cu}(\text{dipy})_2]\text{Cl}_2$ or $[\text{Cu}(\text{gly})_2]$.

Dipyridyl mono(biguanide) copper(II) and o-phenanthroline mono(biguanide) copper(II) etc. :

Development of these complexes with developer II provides two spots : R_f value of one of the spots coincides with that of $[\text{Cu}(\text{dipy})_2]\text{Cl}_2$ or $[\text{Cu}(o\text{-phen})_2]\text{Cl}_2$ in the same developer while the second spot, which diffuses to a long distance, is reminiscent of $[\text{Cu}(\text{BigH})_2]\text{Cl}_2$. A careful visual inspection of the spots of $[\text{Cu}(\text{dipy})(\text{BigH})]\text{Cl}_2$ and $[\text{Cu}(o\text{-phen})(\text{BigH})]\text{Cl}_2$ obtained with developers III and V reveals that although the spots are continuous the chromatographed materials are concentrated towards the ends of the spots (Fig. 4). Developer IV is found to be the suitable one as it alone provides single spots (Fig. 4). So neither too much pyridine (as in developer V) nor too little KCl (as in developer III) can be tolerated.

Effect of substitution in biguanide moiety on R_f values :

We have seen earlier⁵ that on increasing the alkyl substitution on N¹-atom of biguanide the R_f values of the corresponding copper(II), nickel(II) and palladium(II) bis(biguanide) complexes also increase. Similar observation is also noted in the mixed complex systems. R_f value increases from $[\text{Cu}(\text{dipy})(\text{BigH})]\text{Cl}_2$ to $[\text{Cu}(\text{dipy})(\text{Me-BigH})]\text{Cl}_2$ and then to $[\text{Cu}(\text{dipy})(\text{Et-BigH})]\text{Cl}_2$ although this increase is less vigorous compared to the change in the R_f values of bis(biguanide) copper(II) and bis(substituted biguanide) copper(II)⁵.

Concluding Remarks

A good single spot can be obtained with a mixed chelate only when its tendency to disproportionation into the two component homochelates is not too large, and furthermore when a right choice has been made of a developer which can suppress the disproportionation reaction. We wish to emphasize that obtaining two spots out of a mixed chelate cannot be immediately interpreted to mean that the mixed chelate is not a pure single species. Two spots may mean that there is an equilibrium between the mixed chelate and the component homochelates in developer solution and that continued development merely helps in the separation of the two homochelates.

Acknowledgement

This is a pleasure to acknowledge our indebtedness to the CSIR for financial assistance to one of us (R.K.R.)

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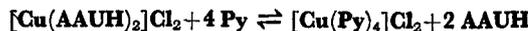
Chromatographic Studies on Metal Complexes. Part III. Paper Chromatography of Square Planar bis (1-amidino- O-alkylurea) Complexes of Copper(II) and Nickel(II)

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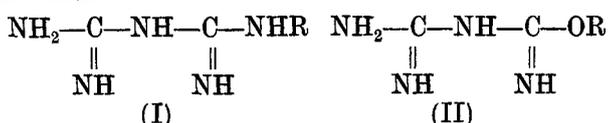
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A paper chromatographic study of a series of square planar bis(1-amidino-O-alkylurea) copper(II)/nickel(II) complexes in aqueous KCl-pyridine developers has been made. R_f values decrease in the order: Ni(II) > Cu(II). Solubilities of the complexes in developers are believed to play a more significant role than the inductive effects of the substituent groups and hydrogen bond forming abilities of the ligand. An equilibrium of the following type



can neither be proved nor dispelled.

BIGUANIDES (BigH; I) and 1-amidino-O-alkylureas (AAUH; II) are closely related ligands^{1,2}. Both the series of ligands provide similar square planar bis(ligand) metal(II) complexes. A paper chromatographic study of bis(1-amidino-O-alkylurea) complexes of copper(II) and nickel(II) in aqueous KCl-pyridine developers is reported in this communication.



[Biguanide, R = H; Alkyl-substituted biguanide, R = alkyl group.]
[1-amidino-O-alkylurea R = alkyl group.]

Methods and Materials

The complexes were obtained by following published procedures^{3,4}. Their purity was checked by elemental analysis and spectral measurement. For the purpose of putting spots copper(II) and nickel(II) complexes of AMUH, AEUH, APⁿUH, APⁱUH (M = methyl; E = ethyl; Pⁿ = *n*-propyl; Pⁱ = isopropyl for R in structure (II)) were dissolved in warm water. The remaining complexes of ABⁿUH, ABⁱUH, AAⁿUH and AAⁱUH (Bⁿ = *n*-butyl; Bⁱ = isobutyl; Aⁿ = *n*-amyl; Aⁱ = isoamyl) were dissolved in ethanol. The following developers were examined:

Developer I : Distilled water (~100 ml)
" II : 100 ml 1(M) KCl
" III : 100 ml 0.5(M)KCl + 5 ml Pyridine
" IV : 100 ml 1(M)KCl + 5 ml Pyridine
" V : 70 ml 0.5(M)KCl + 30 ml (1 : 1)
Pyridine.

Ascending paper chromatography was adopted⁵. For the detection of copper(II) and nickel(II) complexes rubeanic acid in ethanol was found satisfactory. R_f values (Figs. 2 and 3) were reproducible to within $\pm 0.02 R_f$ units. Solubilities (Figs. 1, 2 and 3) were determined by shaking at room temperature (29°-30°) a known excess of the complex salt in a suitable volume of the developer (10, 20 or 25 ml) for 3 hr. The excess was filtered off, washed with a few drops of ice cold water, dried and weighed.

Results and Discussion

We have checked spectrophotometrically that none of the complexes undergoes any drastic change in any of the developers so that they are chromatographed as genuine complexes.

In distilled water (Developer I), the complexes either did not travel at all or diffused to a long distance along the filter paper. Cationic complexes are known to be strongly held on the negatively charged cellulose anion of the filter paper^{5,6,7}. Such strong attraction could be reduced by using developer II. But this developer II was also regarded unsuitable as the spots were too large (16-18 cm). Developer III provided satisfactory spots (~3 cm) for bis(1-amidino-O-alkylurea) complexes of copper (II) only. Unfortunately, this developer provided big sized spots (~7 cm) for bis(1-amidino-O-alkylurea) complexes of nickel(II). Suitable sized spots (2.5-3 cm) of both bis(1-amidino-O-alkylurea) copper (II) and nickel(II) complexes are obtained by using developer IV. With this developer although increasing the chain length of the alkyl substituent led to an increase in the R_f values for copper(II) complexes

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(from methyl upto isopropyl derivatives), no such increase in R_f values was marked for the corresponding nickel(II) complexes.

Effect of alkyl substitution :

In our previous studies⁵ with bis(substituted biguanide) metal(II) complexes we have shown that on increasing the chain length of the alkyl substituent on the N¹-atom of biguanide (I) the R_f values of the corresponding copper(II), nickel(II) and palladium(II) complexes also increase substantially. The two factors, [1] hydrogen bond formation between the cellulose anion and the N¹-atom of biguanide and [2] the inductive effect of the alkyl group were considered responsible for increasing the R_f values. Our previous qualitative conjecture⁵ that on increasing the chain length of the alkyl substituent solubilities of bis(substituted biguanide) metal(II) complexes decrease in aqueous KCl-pyridine developer has now been confirmed on a quantitative basis (Fig. 1).

Thus solubility could not be held responsible for the increasing R_f values with increasing chain length of the substituent in the cases of biguanide complexes.

In the present case of the 1-amidino-O-alkylureas, the hydrogen bond formation remains invariant throughout the series because alkyl substitution does not lead to any decrease of hydrogen atoms in the ligand backbone. As against this, alkyl substitution of the N¹-atom of biguanide does lead to a decrease of the available hydrogen atoms. But the inductive effect of the alkyl group remains. We believe that solubility factor plays here a greater role since the solubility of the copper(II) complexes in aqueous KCl-pyridine (developer IV) is found to increase with increasing chain length of the alkyl substituent (from methyl upto isopropyl derivatives, Fig. 2).

The increase in R_f values of the copper(II) complexes is thus in conformity with the increasing solubility of the complexes to a certain point (isopropyl derivative),

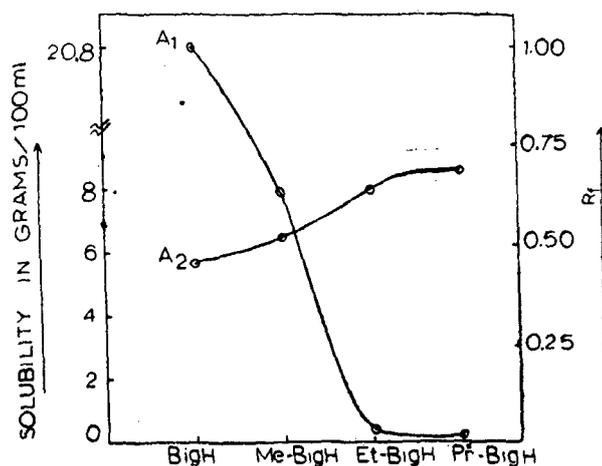


Fig. 1. Variation in solubilities and R_f values of bis(biguanide/substituted biguanide) copper(II) chlorides in developer IV with substitution. A₁, solubility curve; A₂, R_f curve.

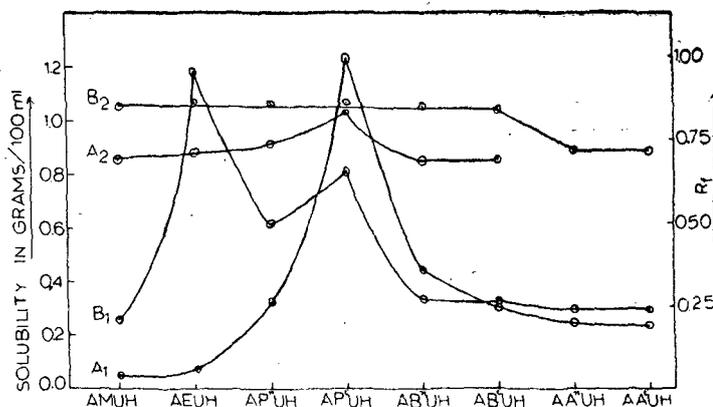
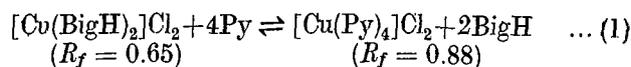


Fig. 2. Variation in solubilities and R_f values of bis(1-amidino-O-alkylurea) copper (II) and nickel(II) chlorides in developer IV with substitution. A₁, solubility curve of copper(II); A₂, R_f curve of copper(II). B₁, solubility curve of nickel(II); B₂, R_f curve of nickel(II).

and thereafter solubilities and R_f values decrease and attain a somewhat steady level.

The solubilities of the nickel(II) complexes pass through two maxima and from isopropyl derivative onwards follow the trend of the corresponding copper(II) complexes although these solubility changes can not influence the R_f values any more because the R_f values have already attained a comparatively high level in the starting compound $[\text{Ni}(\text{AMUH})_2]\text{Cl}_2$ (R_f 0.85, Fig. 2). It is our conviction that changes in solubilities of a family of closely related complexes can influence the R_f values only when they do not start with an already high value. That this suggestion is not entirely unfounded is revealed on an inspection of the R_f values and the solubilities of the complexes in developer V. In this developer, the solubility differences are enormous, (compared to

We have reported earlier⁵ that with higher concentration of pyridine and lower concentration of KCl (developer V) the homochelate $[\text{Cu}(\text{BigH})_2]\text{Cl}_2$ provided two spots which was traced to be due to an equilibrium of the type :



In view of the above results it appeared likely that 1-amidino-O-alkylurea complexes of copper(II) would also provide two spots of substantially different R_f values. We have, however, obtained a single spot which was somewhat bigger in size than shown by $[\text{Cu}(\text{Py})_4]\text{Cl}_2$. In view of the fact that $[\text{Cu}(\text{AMUH})_2]\text{Cl}_2$, $[\text{Cu}(\text{AEUH})_2]\text{Cl}_2$ etc. and $[\text{Cu}(\text{Py})_4]\text{Cl}_2$ exhibit spots with about the same R_f values in this developer

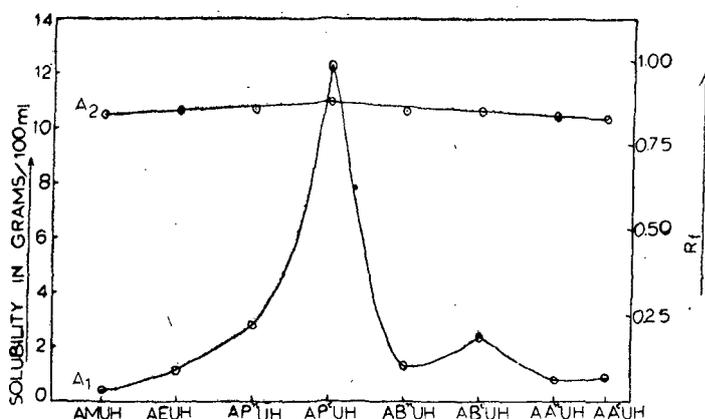


Fig. 3. Variation in solubility and R_f values of bis(1-amidino-O-alkylurea) copper(II) chlorides in developer V with substitution. A_1 , solubility curve; A_2 , R_f curve.

those in developer IV) but the changes in R_f (Fig. 3) are minimal. Note that the starting compound $[\text{Cu}(\text{AMUH})_2]\text{Cl}_2$ has a R_f 0.84 in developer V while its R_f in developer IV is only 0.68. The levelling effect of the R_f values of nickel(II) complexes in developer V is still more apparent since the R_f of starting compound $[\text{Ni}(\text{AMUH})_2]\text{Cl}_2$ is 0.90 instead of 0.85 in developer IV.

Effect of size of the Complexes :

R_f values increase in the order : $\text{Ni} > \text{Cu}$, in the order of decreasing size and weight : $\text{Ni} < \text{Cu}$ (Fig. 2).

Effect of KCl/pyridine :

Like bis(biguanide) and bis(substituted biguanide) complexes of copper(II) and nickel(II), R_f values of bis(1-amidino-O-alkylurea) complexes of copper(II) and nickel(II) also increase on increasing the KCl concentration in aqueous KCl-pyridine developer. It is to be noted that neither KCl nor pyridine alone can give good spots. With lower concentration of KCl and higher concentration of pyridine (developer V) all the complexes provided good spots (~ 1 cm) and higher R_f values compared to those with developer IV. This is also due to increased solubility of the complexes in this developer (Figs. 2 and 3).

it is not unlikely that the two expected spots have got fused together. Equilibrium of type (1), therefore, has neither been definitely established nor dispelled in the case of bis(1-amidino-O-alkylurea) copper(II) complexes.

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