# 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. [Cu(gly)(BigH)]Cl, [Cu(α-alan)(BigH)]Cl etc. give two spots in all the developers studied. An equilibrium of the following type is suggested :

$$2[Cu(gly)(BigH)]Cl \rightleftharpoons [Cu(gly)_2] + [Cu(BigH)]_2Cl_2$$
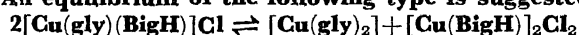
[Cu(gly)(o-phen)[Cl also shows similar behaviour. Such disproportionation reaction is less favoured in [Cu(gly)(dipy)]Cl. [Cu(o-phen)(BigH)]Cl_2 and [Cu(dipy)(BigH\)]Cl_2 provide single spot on proper choice of the developer.

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).
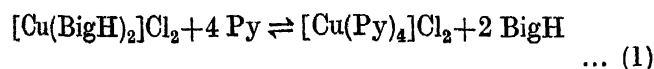
Methods and Materials

The mixed chelates were obtained by following published procedures[1-4]. Their purity was checked by elemental analysis and spectral measurements. Ascending paper chromatography was adopted. Experimental techniques have been described elsewhere[5]. 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 ± 0.02 R_f units.

Results and Discussion

We have reported earlier[5] that with higher concentration of pyridine and low concentration of KCl (as in developer V), the homochelate [Cu(BigH)_2]Cl_2 provided two spots, which was traced to be due to an equilibrium of the type :

$$[Cu(BigH)_2]Cl_2 + 4 Py \rightleftharpoons [Cu(Py)_4]Cl_2 + 2 BigH \quad \dots (1)$$

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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	[Cu(dipy)(IDA)]	0.87
	[Cu(o-phen)(IDA)]	0.80
	[Cu(BigH)(IDA)]	0.70
+1	[Cu(gly)(BigH)]Cl	0.53, 0.93
	[Cu(gly)(Me-BigH)]Cl	0.60, 0.93
	[Cu(gly)(Et-BigH)]Cl	0.66, 0.93
	[Cu(α-alan)(BigH)]Cl	0.53, 0.94
	[Cu(α-alan)(Me-BigH)]Cl	0.60, 0.94
	[Cu(α-lan)(Et-BigH)]Cl	0.66, 0.94
	[Cu(gly)(o-phen)]Cl	0.80, 0.91
	[Cu(gly)(dipy)]Cl	0.80
+2	[Cu(dipy)(BigH)]Cl_2	0.74
	[Cu(dipy)(Me-BigH)]Cl_2	0.77
	[Cu(dipy)(Et-BigH)]Cl_2	0.81
	[Cu(o-phen)(BigH)]Cl_2	0.71

Under similar condition R_f values of the homochelates are : [Cu(gly)_2] = 0.93; [Cu(α-alan)_2] = 0.94; [Cu(BigH)_2]Cl_2 = 0.53; [Cu(Me-BigH)_2]Cl_2 = 0.60; [Cu(Et-BigH)_2]Cl_2 = 0.66; [Cu(dipy)_2]Cl_2 = 0.91; [Cu(o-phen)_2]Cl_2 = 0.80; gly H = glycine; α-alanH = α-alanine; BigH = biguanide; Me-BigH = methyl biguanide; Et-BigH = ethyl biguanide; dipy = dipyridyl; o-phen = orthophenanthroline; IDAH_2 = iminodiacetic acid.

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 paper[6]. 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)]Cl$_2$, [Cu(dipy)(Me-BigH)]Cl$_2$, [Cu(dipy)-(Et-BigH)]Cl$_2$, 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 :

$$[Cu(dipy)(IDA)] > [Cu(o\text{-phen})(IDA)] > [Cu(BigH)\text{-}(IDA)].$$
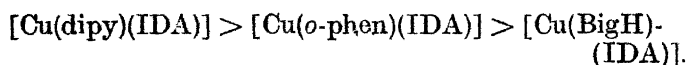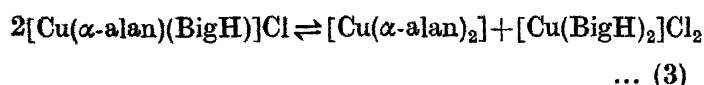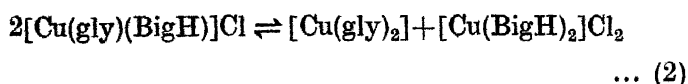
This order is also the order of increasing solubility of the complexes in aqueous KCl—pyridine developer. The mixed chelates seem to possess non-electrolytic nature rather than the electrolytic structure e.g., [Cu(dipy)$_2$][Cu(IDA)$_2$]. etc. The electrolytic structure would admit of two spots.

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

Das Sarma and Ray noted[3] 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 :

$$2[Cu(gly)(BigH)]Cl \rightleftharpoons [Cu(gly)_2] + [Cu(BigH)_2]Cl_2 \qquad ... (2)$$

$$2[Cu(\alpha\text{-alan})(BigH)]Cl \rightleftharpoons [Cu(\alpha\text{-alan})_2] + [Cu(BigH)_2]Cl_2 \qquad ... (3)$$

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).
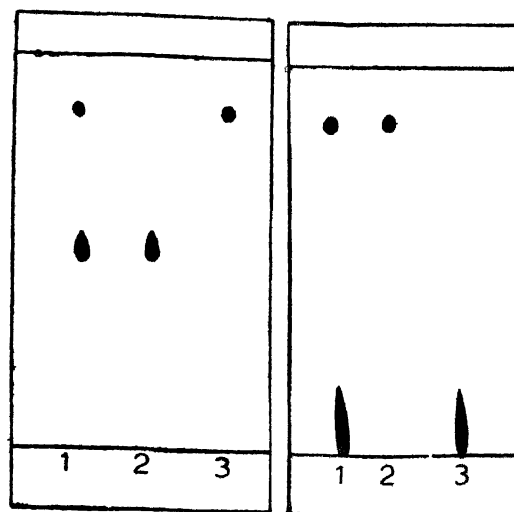

Fig. 1.   Fig. 2.

Fig. 1. Chromatograms in 100 ml 1(M) KCl+5 ml Pyridine as developer (Developer IV).
(1) [Cu(gly)(BigH)]Cl;   (2) [Cu(BigH)$_2$]Cl$_2$;
(3) [Cu(gly)$_2$].

Fig. 2. Chromatograms in 100 ml distilled water as developer (Developer I)
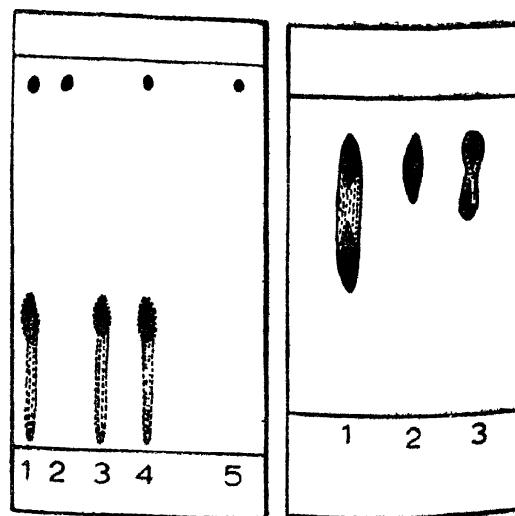(1) [Cu(gly)(BigH)]Cl; (2) [Cu(gly)$_2$]; (3) [Cu(BigH)$_2$]Cl$_2$

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)$_2$]Cl$_2$;   (4) [Cu(α-alan)(BigH)]Cl;
(5) [Cu(α-alan)$_2$].

Fig. 4. Chromatograms of [Cu(o-phen)(BigH)]Cl$_2$ 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 studies[5] of [Cu(BigH)$_2$]Cl$_2$ in developer V we had reported chromatographic evidence in favour of equilibrium(1). One would therefore expect three spots of [Cu(gly)(BigH)]Cl in developer V, resulting from a secondary equilibrium of [Cu (BigH)$_2$]Cl$_2$ with large excess of pyridine present in developer(V) giving another species [Cu(Py)$_4$]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 [Cu(gly)$_2$] and [Cu(Py)$_4$]Cl$_2$ show almost the same R$_f$ in this developer ([Cu(gly)$_2$] = 0.85; [Cu(Py)$_4$]Cl$_2$ = 0.86).

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

[Cu(gly)(dipy)]Cl provides, in developer IV, single spot with R$_f$ = 0.80 while [Cu(gly)(o-phen)]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 [Cu(gly)$_2$]. The R$_f$ value of [Cu(o-phen)$_2$]Cl$_2$ is also around 0.80. So the following disproportionation reaction is suggested :

$$2[Cu(gly)(o\text{-phen})]Cl \rightleftharpoons [Cu(gly)_2]+[Cu(o\text{-phen})_2]Cl_2$$
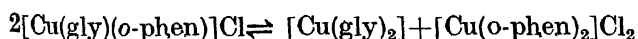
Similar disproportionation of [Cu(gly)(dipy)]Cl into two homochelates is less favoured since we get one spot with R$_f$ = 0.80 which is different from that of either [Cu(dipy)$_2$]Cl$_2$ or [Cu(gly)$_2$].

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 [Cu(dipy)$_2$]Cl$_2$ or [Cu(o-phen)$_2$]Cl$_2$ in the same developer while the second spot, which diffuses to a long distance, is reminiscent of [Cu (BigH)$_2$]Cl$_2$. A careful visual inspection of the spots of [Cu(dipy)(BigH)]Cl$_2$ and [Cu(o-phen)(BigH)]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 earlier[5] that on increasing the 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. Similar observation is also noted in the mixed complex systems. R$_f$ value increases from [Cu(dipy)-(BigH)]Cl$_2$ to [Cu(dipy)(Me-BigH)]Cl$_2$ and then to [Cu(dipy)(Et-BigH)]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

References

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