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## A RADIOCHROMATOGRAPHIC STUDY OF SOME ETHYLTHIOUREA COMPLEXES OF COPPER(I), SILVER(I) AND GOLD(I)

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### SUMMARY

Some ethylthiourea (Etu) complexes of copper(I), silver(I) and gold(I) migrate, with a definite and stable metal-Etu ratio, on paper during development with aqueous solutions of the sodium salt of the same anion at different concentrations (0.5–5.0 *M*). The metal-Etu ratios of such complexes were radiochemically determined by using <sup>35</sup>S-labelled Etu, which instantaneously and completely exchanged with the complexed Etu. The stable migrating complexes have, for each system, a constant metal-Etu ratio, irrespective of the initial ratio in the complex and independent of the sodium salt concentration in the developing solvent. In systems containing perchlorate or fluoroborate, both copper(I) and silver(I) form a stable migrating 1:2 complex; in the presence of trifluoroacetate, silver(I) forms a 2:3 complex, probably involving the trifluoroacetate anion; in chloride- or bromide-containing systems, copper(I) forms a 1:1 complex in which the halide participates in the coordination, whereas silver(I) forms a 1:1 complex in chloride solution, but no definite complex in bromide solution because of the strong competitive coordinating action of Etu. Gold(I) forms only a 1:2 complex, irrespective of the initial ratio of gold to Etu, the anion and its concentration in the developing solution. *R<sub>F</sub>* values of the migrating species are discussed.

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### INTRODUCTION

In previous work, we have demonstrated by radiochromatographic methods that the thiourea complexes of palladium(II) and platinum(II)<sup>1</sup>, of zinc(II), cadmium(II) and mercury(II)<sup>2</sup>, and of copper(I), silver(I) and gold(I)<sup>3</sup>, and the ethylthiourea (Etu) complexes of palladium(II) and platinum(II)<sup>4</sup>, migrate on paper strips in compact spots of definite composition. The silver(I)-Etu<sup>5</sup> and copper(I)-Etu<sup>6</sup> complexes have been studied by conductometric and high-frequency titration.

Several Etu complexes of copper(I), silver(I) and gold(I) have been prepared and studied by conductometric methods and infrared spectroscopy, and the results will be described elsewhere. These complexes have been now investigated by the radiochromatographic methods described previously<sup>1-4</sup>, aqueous solutions<sup>5</sup> of the corresponding sodium salt at various concentrations being used as developing solvent.

TABLE I

PAPER CHROMATOGRAPHY OF COPPER(I) COMPLEXES WITH ETHYLTHIOUREA (Etu) ADDED WITH FREE  $^{35}\text{S}$ -ETHYLTHIOUREA (Etu\*) IN AQUEOUS 0.5-5 M SOLUTIONS OF THE CORRESPONDING SODIUM SALT (NaA)

Anion (A)	Aqueous solution of NaA (M)	Migrating species	Etu* complexed (%)	Etu* free (%)	Cu:Etu in complex	$R_f$	
						Complex	Etu
$\text{ClO}_4^-$	0.5	$\text{Cu}_2\text{Etu}_3^{2+} + 3\text{Etu}^*$	No separation				
	1	$\text{Cu}_2\text{Etu}_3^{2+} + 3\text{Etu}^*$	65.06	34.94	1:2	0.37	0.78
	2	$\text{Cu}_2\text{Etu}_3^{2+} + 3\text{Etu}^*$	67.71	32.29	1:2	0.23	0.80
	3	$\text{Cu}_2\text{Etu}_3^{2+} + 3\text{Etu}^*$	66.36	33.64	1:2	0.11	0.80
	4	$\text{Cu}_2\text{Etu}_3^{2+} + 3\text{Etu}^*$	66.79	33.21	1:2	0.00	0.80
	5	$\text{Cu}_2\text{Etu}_3^{2+} + 3\text{Etu}^*$	66.51	33.49	1:2	0.00	0.80
	0.5	$\text{CuEtu}_3^+ + 3\text{Etu}^*$	No separation				
	1	$\text{CuEtu}_3^+ + 3\text{Etu}^*$	33.35	66.65	1:2	0.40	0.79
	2	$\text{CuEtu}_3^+ + 3\text{Etu}^*$	32.34	67.66	1:2	0.23	0.80
	3	$\text{CuEtu}_3^+ + 3\text{Etu}^*$	34.15	65.85	1:2	0.11	0.80
$\text{BF}_4^-$	0.5-2	$\text{Cu}_2\text{Etu}_3^{2+} + 3\text{Etu}^*$	No separation				
	3	$\text{Cu}_2\text{Etu}_3^{2+} + 3\text{Etu}^*$	67.03	32.97	1:2	0.55	0.67
	4	$\text{Cu}_2\text{Etu}_3^{2+} + 3\text{Etu}^*$	66.53	33.47	1:2	0.28	0.58
	5	$\text{Cu}_2\text{Etu}_3^{2+} + 3\text{Etu}^*$	66.04	33.96	1:2	0.28	0.58
	0.5-2	$\text{Cu}_2\text{Etu}_5^{2+} + 5\text{Etu}^*$	No separation				
	3	$\text{Cu}_2\text{Etu}_5^{2+} + 5\text{Etu}^*$	41.55	58.45	1:2	0.58	0.70
	4	$\text{Cu}_2\text{Etu}_5^{2+} + 5\text{Etu}^*$	39.76	60.24	1:2	0.25	0.58
	5	$\text{Cu}_2\text{Etu}_5^{2+} + 5\text{Etu}^*$	39.41	60.59	1:2	0.28	0.59
	0.5-2	$\text{CuEtu}_3^+ + 3\text{Etu}^*$	No separation				
	3	$\text{CuEtu}_3^+ + 3\text{Etu}^*$	34.33	65.67	1:2	0.55	0.69
4	$\text{CuEtu}_3^+ + 3\text{Etu}^*$	33.93	66.07	1:2	0.27	0.58	
5	$\text{CuEtu}_3^+ + 3\text{Etu}^*$	33.83	66.17	1:2	0.26	0.58	
$\text{CF}_3\text{COO}^-$	0.5-5	$\text{Cu}_2\text{Etu}_3^{2+} + 3\text{Etu}^*$	No separation				
	0.5-5	$\text{CuEtu}_3^+ + 3\text{Etu}^*$	No separation				
$\text{Cl}^-$	0.5-1	$\text{CuEtu}^+ + \text{Etu}^*$	No Separation				
	2	$\text{CuEtu}^+ + \text{Etu}^*$	49.38	50.62	1:1	0.19	0.72
	3	$\text{CuEtu}^+ + \text{Etu}^*$	49.60	50.40	1:1	0.11	0.72
	4	$\text{CuEtu}^+ + \text{Etu}^*$	50.13	49.87	1:1	0.10	0.70
	5	$\text{CuEtu}^+ + \text{Etu}^*$	50.15	49.85	1:1	0.11	0.70
	0.5-1	$\text{CuEtu}_2^+ + 2\text{Etu}^*$	No separation				
	2	$\text{CuEtu}_2^+ + 2\text{Etu}^*$	25.43	74.57	1:1	0.25	0.72
	3	$\text{CuEtu}_2^+ + 2\text{Etu}^*$	25.51	74.49	1:1	0.14	0.73
	4	$\text{CuEtu}_2^+ + 2\text{Etu}^*$	24.07	75.93	1:1	0.14	0.75
	5	$\text{CuEtu}_2^+ + 2\text{Etu}^*$	24.46	75.54	1:1	0.14	0.71
	0.5-1	$\text{Cu}_2\text{Etu}_5^{2+} + 5\text{Etu}^*$	No separation				
	2	$\text{Cu}_2\text{Etu}_5^{2+} + 5\text{Etu}^*$	19.57	80.43	1:1	0.22	0.74
	3	$\text{Cu}_2\text{Etu}_5^{2+} + 5\text{Etu}^*$	19.31	80.69	1:1	0.12	0.75
	4	$\text{Cu}_2\text{Etu}_5^{2+} + 5\text{Etu}^*$	20.38	79.62	1:1	0.11	0.73
	5	$\text{Cu}_2\text{Etu}_5^{2+} + 5\text{Etu}^*$	19.74	80.26	1:1	0.13	0.72
0.5-1	$\text{CuEtu}_3^+ + 3\text{Etu}^*$	No separation					
2	$\text{CuEtu}_3^+ + 3\text{Etu}^*$	16.23	83.77	1:1	0.23	0.74	
3	$\text{CuEtu}_3^+ + 3\text{Etu}^*$	16.31	83.69	1:1	0.12	0.75	
4	$\text{CuEtu}_3^+ + 3\text{Etu}^*$	16.07	83.93	1:1	0.12	0.75	
5	$\text{CuEtu}_3^+ + 3\text{Etu}^*$	16.64	83.36	1:1	0.11	0.72	

TABLE I (continued)

Anion (A)	Aqueous solution of NaA (M)	Migrating species	Etu*		Cu:Etu in complex	R <sub>F</sub>	
			complexed (%)	free (%)		Complex	Etu
Br <sup>-</sup>	0.5	CuEtu <sup>+</sup> + Etu*	50.16	49.84	1:1	0.19	0.65
	1	CuEtu <sup>+</sup> + Etu*	50.66	49.34	1:1	0.19	0.66
	2	CuEtu <sup>+</sup> + Etu*	50.54	49.45	1:1	0.15	0.67
	3	CuEtu <sup>+</sup> + Etu*	49.89	50.11	1:1	0.14	0.65
	4	CuEtu <sup>+</sup> + Etu*	50.55	49.45	1:1	0.14	0.69
	5	CuEtu <sup>+</sup> + Etu*	49.34	50.66	1:1	0.14	0.69
	0.5	CuEtu <sub>2</sub> <sup>+</sup> + 2Etu*	24.51	75.49	1:1	0.27	0.75
	1	CuEtu <sub>2</sub> <sup>+</sup> + 2Etu*	24.85	75.15	1:1	0.27	0.75
	2	CuEtu <sub>2</sub> <sup>+</sup> + 2Etu*	25.23	74.77	1:1	0.27	0.74
	3	CuEtu <sub>2</sub> <sup>+</sup> + 2Etu*	24.90	75.10	1:1	0.24	0.76
	4	CuEtu <sub>2</sub> <sup>+</sup> + 2Etu*	25.05	74.95	1:1	0.26	0.78
	5	CuEtu <sub>2</sub> <sup>+</sup> + 2Etu*	25.38	74.62	1:1	0.26	0.77
	0.5	Cu <sub>2</sub> Etu <sub>5</sub> <sup>2+</sup> + 5Etu*	20.25	79.75	1:1	0.26	0.75
	1	Cu <sub>2</sub> Etu <sub>5</sub> <sup>2+</sup> + 5Etu*	20.48	79.52	1:1	0.24	0.75
	2	Cu <sub>2</sub> Etu <sub>5</sub> <sup>2+</sup> + 5Etu*	20.79	79.21	1:1	0.24	0.74
	3	Cu <sub>2</sub> Etu <sub>5</sub> <sup>2+</sup> + 5Etu*	20.68	79.32	1:1	0.23	0.76
	4	Cu <sub>2</sub> Etu <sub>5</sub> <sup>2+</sup> + 5Etu*	19.38	80.62	1:1	0.24	0.77
	5	Cu <sub>2</sub> Etu <sub>5</sub> <sup>2+</sup> + 5Etu*	19.53	80.47	1:1	0.25	0.77
	0.5	CuEtu <sub>3</sub> <sup>+</sup> + 3Etu*	16.99	83.01	1:1	0.27	0.75
	1	CuEtu <sub>3</sub> <sup>+</sup> + 3Etu*	17.08	82.92	1:1	0.25	0.75
	2	CuEtu <sub>3</sub> <sup>+</sup> + 3Etu*	15.97	84.03	1:1	0.24	0.74
	3	CuEtu <sub>3</sub> <sup>+</sup> + 3Etu*	16.32	83.68	1:1	0.23	0.74
	4	CuEtu <sub>3</sub> <sup>+</sup> + 3Etu*	16.60	83.40	1:1	0.26	0.77
	5	CuEtu <sub>3</sub> <sup>+</sup> + 3Etu*	16.51	83.49	1:1	0.26	0.77

## EXPERIMENTAL

The solid Etu complexes of copper(I), silver(I) and gold(I) prepared by us are characterized in Table IV by their ratios of Etu to metal; some of them were used for the radiochromatographic investigations. The complexes AuEtu<sub>2</sub>ClO<sub>4</sub> and AuEtu<sub>2</sub>CF<sub>3</sub>COO could not be isolated in the solid state, but only in solution; the solid AuEtu<sub>2</sub>Cl complex was dissolved in aqueous perchloric acid or trifluoroacetic acid, the solution was evaporated to dryness with gentle heating, the residue was dissolved in the appropriate acid, and this solution was evaporated to dryness. Each final residue was dissolved in water to give a solution 0.1 M in Etu.

The paper chromatography of the complexes was performed at room temperature, with a developing solvent consisting of an aqueous solution of the sodium salt (0.5–5.0 M) of the anion contained in the complex. In these conditions, both the complex and Etu migrate independently in compact and separate spots. The migrating species were identified as follows: (a) Etu by using an aqueous solution of iodine-potassium iodide or with Roche reagent<sup>7</sup>; (b) copper(I), silver(I) and gold(I) by suspending the moist paper strips in an atmosphere of hydrogen sulphide, which gives black-brown spots. Both the Etu and metal-ion spots gave R<sub>F</sub> values.

For the radiochromatographic measurements, equal volumes of 0.1 M solutions of <sup>35</sup>S-labelled Etu (Etu\*) and the complexes (0.1 M in Etu) in acidic

TABLE II

PAPER CHROMATOGRAPHY OF SILVER(I) COMPLEXES WITH ETHYLTHIOUREA (Etu) ADDED WITH FREE  $^{35}\text{S}$ -ETHYLTHIOUREA (Etu\*) IN 0.5-5 M SOLUTIONS OF THE CORRESPONDING SODIUM SALT (NaA)

Anion (A)	Aqueous solution of NaA (M)	Migrating species	Etu* complexed (%)	Etu* free (%)	Ag:Etu in complex	R <sub>F</sub> Complex	R <sub>F</sub> Etu
ClO <sub>4</sub> <sup>-</sup>	0.5	AgEtu <sup>+</sup> + Etu*	100	—	1:2	0.30	—
	1	AgEtu <sup>+</sup> + Etu*	100	—	1:2	0.24	—
	2	AgEtu <sup>+</sup> + Etu*	100	—	1:2	0.12	—
	3	AgEtu <sup>+</sup> + Etu*	100	—	1:2	0.04	—
	4	AgEtu <sup>+</sup> + Etu*	100	—	1:2	0.00	—
	5	AgEtu <sup>+</sup> + Etu*	100	—	1:2	0.00	—
	0.5	Ag <sub>2</sub> Etu <sub>3</sub> <sup>2+</sup> + 3Etu*	No separation				
	1	Ag <sub>2</sub> Etu <sub>3</sub> <sup>2+</sup> + 3Etu*	66.12	33.88	1:2	0.29	0.79
	2	Ag <sub>2</sub> Etu <sub>3</sub> <sup>2+</sup> + 3Etu*	65.93	34.07	1:2	0.13	0.80
	3	Ag <sub>2</sub> Etu <sub>3</sub> <sup>2+</sup> + 3Etu*	66.26	33.74	1:2	0.06	0.80
	4	Ag <sub>2</sub> Etu <sub>3</sub> <sup>2+</sup> + 3Etu*	66.36	33.64	1:2	0.00	0.78
	5	Ag <sub>2</sub> Etu <sub>3</sub> <sup>2+</sup> + 3Etu*	66.77	33.23	1:2	0.00	0.76
	0.5	AgEtu <sub>2</sub> <sup>+</sup> + 2Etu*	No separation				
	1	AgEtu <sub>2</sub> <sup>+</sup> + 2Etu*	49.79	50.21	1:2	0.27	0.79
	2	AgEtu <sub>2</sub> <sup>+</sup> + 2Etu*	50.45	49.55	1:2	0.14	0.78
	3	AgEtu <sub>2</sub> <sup>+</sup> + 2Etu*	49.17	50.83	1:2	0.04	0.80
	4	AgEtu <sub>2</sub> <sup>+</sup> + 2Etu*	49.18	50.82	1:2	0.00	0.79
	5	AgEtu <sub>2</sub> <sup>+</sup> + 2Etu*	49.78	50.22	1:2	0.00	0.77
	0.5	AgEtu <sub>3</sub> <sup>+</sup> + 3Etu*	No separation				
	1	AgEtu <sub>3</sub> <sup>+</sup> + 3Etu*	32.87	67.13	1:2	0.26	0.79
	2	AgEtu <sub>3</sub> <sup>+</sup> + 3Etu*	32.80	67.20	1:2	0.12	0.80
	3	AgEtu <sub>3</sub> <sup>+</sup> + 3Etu*	34.55	65.45	1:2	0.03	0.78
	4	AgEtu <sub>3</sub> <sup>+</sup> + 3Etu*	33.15	66.85	1:2	0.00	0.80
	5	AgEtu <sub>3</sub> <sup>+</sup> + 3Etu*	32.09	67.91	1:2	0.00	0.79
	BF <sub>4</sub> <sup>-</sup>	0.5	AgEtu <sup>+</sup> + Etu*	100	—	1:2	0.78
1		AgEtu <sup>+</sup> + Etu*	100	—	1:2	0.75	—
2		AgEtu <sup>+</sup> + Etu*	100	—	1:2	0.53	—
3		AgEtu <sup>+</sup> + Etu*	100	—	1:2	0.32	—
4		AgEtu <sup>+</sup> + Etu*	100	—	1:2	0.10	—
5		AgEtu <sup>+</sup> + Etu*	100	—	1:2	0.00	—
0.5-2		Ag <sub>2</sub> Etu <sub>3</sub> <sup>2+</sup> + 3Etu*	No separation				
3		Ag <sub>2</sub> Etu <sub>3</sub> <sup>2+</sup> + 3Etu*	66.66	33.33	1:2	0.43	0.68
4		Ag <sub>2</sub> Etu <sub>3</sub> <sup>2+</sup> + 3Etu*	66.21	33.79	1:2	0.10	0.59
5		Ag <sub>2</sub> Etu <sub>3</sub> <sup>2+</sup> + 3Etu*	66.68	33.32	1:2	0.00	0.58
0.5-2		AgEtu <sub>3</sub> <sup>+</sup> + 3Etu*	No separation				
3		AgEtu <sub>3</sub> <sup>+</sup> + 3Etu*	33.68	66.32	1:2	0.46	0.67
4		AgEtu <sub>3</sub> <sup>+</sup> + 3Etu*	33.46	66.54	1:2	0.14	0.57
5		AgEtu <sub>3</sub> <sup>+</sup> + 3Etu*	33.83	66.17	1:2	0.00	0.56
CF <sub>3</sub> COO <sup>-</sup>		0.5-2	AgEtu <sup>+</sup> + Etu*	No separation			
	3	AgEtu <sup>+</sup> + Etu*	75.31	24.69	2:3	0.10	0.73
	4	AgEtu <sup>+</sup> + Etu*	75.14	24.86	2:3	0.00	0.74
	5	AgEtu <sup>+</sup> + Etu*	74.37	25.63	2:3	0.00	0.75
	0.5-1	Ag <sub>2</sub> Etu <sub>3</sub> <sup>2+</sup> + 3Etu*	No separation				
	2	Ag <sub>2</sub> Etu <sub>3</sub> <sup>2+</sup> + 3Etu*	49.45	50.55	2:3	0.30	0.73
	3	Ag <sub>2</sub> Etu <sub>3</sub> <sup>2+</sup> + 3Etu*	50.46	49.54	2:3	0.10	0.74
	4	Ag <sub>2</sub> Etu <sub>3</sub> <sup>2+</sup> + 3Etu*	49.52	50.48	2:3	0.00	0.75

TABLE II (continued)

Anion (A)	Aqueous solution of NaA (M)	Migrating species	Etu* complexed (%)	Etu* free (%)	Ag:Etu in complex	$R_F$	
						Complex	Etu
Cl <sup>-</sup>	5	Ag <sub>2</sub> Etu <sub>3</sub> <sup>2+</sup> + 3Etu*	49.82	50.18	2:3	0.00	0.76
	0.5-2	AgEtu <sub>3</sub> <sup>+</sup> + 3Etu*	No separation				
	3	AgEtu <sub>3</sub> <sup>+</sup> + 3Etu*	24.59	75.41	2:3	0.10	0.75
	4	AgEtu <sub>3</sub> <sup>+</sup> + 3Etu*	24.70	75.30	2:3	0.00	0.76
	5	AgEtu <sub>3</sub> <sup>+</sup> + 3Etu*	25.18	74.82	2:3	0.00	0.77
	0.5	AgEtu <sup>+</sup> + Etu*	49.57	50.43	1:1	0.13	0.76
	1	AgEtu <sup>+</sup> + Etu*	49.24	50.76	1:1	0.13	0.75
	2	AgEtu <sup>+</sup> + Etu*	50.63	49.37	1:1	0.15	0.74
	3	AgEtu <sup>+</sup> + Etu*	50.84	49.16	1:1	0.15	0.73
	4	AgEtu <sup>+</sup> + Etu*	49.93	50.07	1:1	0.15	0.74
	5	AgEtu <sup>+</sup> + Etu*	49.95	50.05	1:1	0.16	0.73
	0.5	AgEtu <sub>3</sub> <sup>+</sup> + 3Etu*	17.22	82.78	1:1	0.14	0.76
	1	AgEtu <sub>3</sub> <sup>+</sup> + 3Etu*	16.58	83.35	1:1	0.14	0.77
	2	AgEtu <sub>3</sub> <sup>+</sup> + 3Etu*	16.33	83.66	1:1	0.13	0.77
	3	AgEtu <sub>3</sub> <sup>+</sup> + 3Etu*	16.90	83.10	1:1	0.15	0.76
4	AgEtu <sub>3</sub> <sup>+</sup> + 3Etu*	16.02	83.98	1:1	0.15	0.73	
5	AgEtu <sub>3</sub> <sup>+</sup> + 3Etu*	16.56	83.44	1:1	0.15	0.72	
Br <sup>-</sup>	0.5	AgEtu <sup>+</sup> + Etu*	35.56	64.44			
	1	AgEtu <sup>+</sup> + Etu*	33.29	66.71			
	2-5	AgEtu <sup>+</sup> + Etu*	No separation				
	0.5	AgEtu <sub>3</sub> <sup>+</sup> + 3Etu*	12.14	87.86			
	1	AgEtu <sub>3</sub> <sup>+</sup> + 3Etu*	11.85	88.15			
	2-5	AgEtu <sub>3</sub> <sup>+</sup> + 3Etu*	No separation				

methanol for the perchlorates, fluoroborates and trifluoroacetates and in acidic dimethylformamide for the halides, were so mixed as to give a molar ratio of complexed Etu to free Etu\* of 1:1. A 10- $\mu$ l portion of each of these solutions was transferred to a strip of Whatman No. 1 paper (1  $\times$  35 cm) and, after being dried at room temperature, developed under the above-mentioned conditions with the solvents listed in Tables I, II and III. The dried chromatograms were quantitatively scanned in a stepwise manner with a Geiger-Müller counter. The sum of the measured radioactivities for the complex and the Etu spots was always equal to the activity of the original spot before elution.

Since the exchange of complexed Etu and free Etu\* in solution is instantaneous and complete, the stoichiometry of the migrating complex was obtained from the ratio of the activities of each spot and the total original activity by using the equation:

$$[\text{MEtu}_x]^+ + x\text{Etu}^* = [\text{MEtu}_y]^+ + (2x - y)\text{Etu}^*$$

## RESULTS AND DISCUSSION

The radiochromatographic results are reported in Table I for copper(I), Table II for silver(I) and Table III for gold(I). The use of different ratios of metal to Etu and developing with aqueous solutions of the corresponding sodium salt of the

appropriate anion resulted in the formation of only one complex stable in the conditions of development.

With the perchlorate and fluoroborate anions, which have very low co-ordinating tendencies, only the 1:2 complexes of the three metal ions were stable. As it is most improbable that, in aqueous solution, these anions are co-ordinated to the metal, and since the tendency of monovalent ions of the IB group to be solvated by water is very low, it is probable that these 1:2 complexes have a linear structure  $[\text{MEtu}_2]^+$  with sp coordination; a dimer Etu-bridged structure  $[\text{M}_2\text{Etu}_4]^{2+}$  seems less probable.

The trifluoroacetate anion, which has a greater tendency to co-ordinate than have the former two anions, shows different behaviour. With silver(I), it forms a 2:3

TABLE III

PAPER CHROMATOGRAPHY OF GOLD(I) COMPLEXES WITH ETHYLTHIOUREA (Etu) ADDED WITH FREE  $^{35}\text{S}$ -ETHYLTHIOUREA (Etu\*) IN 0.5-5 M AQUEOUS SOLUTIONS OF THE CORRESPONDING SODIUM SALT (NaA)

Anion (A)	Aqueous solution of NaA (M)	Migrating species	Etu*	Etu*	Au:Etu in complex	$R_F$	
			complexed (%)	free (%)		Complex	Etu
$\text{ClO}_4^-$	0.5	$\text{AuEtu}_2^+ + 2\text{Etu}^*$	50.12	49.88	1:2	0.53	0.78
	1	$\text{AuEtu}_2^+ + 2\text{Etu}^*$	49.80	50.20	1:2	0.48	0.80
	2	$\text{AuEtu}_2^+ + 2\text{Etu}^*$	50.00	50.00	1:2	0.39	0.81
	3	$\text{AuEtu}_2^+ + 2\text{Etu}^*$	50.07	49.93	1:2	0.38	0.80
	4	$\text{AuEtu}_2^+ + 2\text{Etu}^*$	50.18	49.82	1:2	0.34	0.80
$\text{BF}_4^-$	0.5	$\text{AuEtu}_2^+ + 2\text{Etu}^*$	49.99	50.01	1:2	0.56	0.77
	1	$\text{AuEtu}_2^+ + 2\text{Etu}^*$	50.06	49.94	1:2	0.50	0.75
	2	$\text{AuEtu}_2^+ + 2\text{Etu}^*$	50.10	49.90	1:2	0.39	0.72
	3	$\text{AuEtu}_2^+ + 2\text{Etu}^*$	49.81	50.19	1:2	0.29	0.67
	4	$\text{AuEtu}_2^+ + 2\text{Etu}^*$	49.78	50.22	1:2	0.19	0.64
$\text{CF}_3\text{COO}^-$	0.5	$\text{AuEtu}_2^+ + 2\text{Etu}^*$	50.11	49.89	1:2	0.58	0.76
	1	$\text{AuEtu}_2^+ + 2\text{Etu}^*$	50.26	49.74	1:2	0.57	0.75
	2	$\text{AuEtu}_2^+ + 2\text{Etu}^*$	49.83	50.17	1:2	0.46	0.75
	3	$\text{AuEtu}_2^+ + 2\text{Etu}^*$	49.80	50.20	1:2	0.43	0.75
	4	$\text{AuEtu}_2^+ + 2\text{Etu}^*$	50.08	49.92	1:2	0.43	0.76
$\text{Cl}^-$	0.5	$\text{AuEtu}_2^+ + 2\text{Etu}^*$	49.99	50.01	1:2	0.50	0.76
	1	$\text{AuEtu}_2^+ + 2\text{Etu}^*$	50.01	49.99	1:2	0.44	0.76
	2	$\text{AuEtu}_2^+ + 2\text{Etu}^*$	49.93	50.07	1:2	0.39	0.77
	3	$\text{AuEtu}_2^+ + 2\text{Etu}^*$	49.98	50.02	1:2	0.34	0.77
	4	$\text{AuEtu}_2^+ + 2\text{Etu}^*$	49.66	50.34	1:2	0.24	0.77
$\text{Br}^-$	0.5	$\text{AuEtu}_2^+ + 2\text{Etu}^*$	49.24	50.76	1:2	0.53	0.76
	1	$\text{AuEtu}_2^+ + 2\text{Etu}^*$	50.28	49.72	1:2	0.52	0.78
	2	$\text{AuEtu}_2^+ + 2\text{Etu}^*$	50.09	49.01	1:2	0.50	0.80
	3	$\text{AuEtu}_2^+ + 2\text{Etu}^*$	49.44	50.56	1:2	0.48	0.82
	4	$\text{AuEtu}_2^+ + 2\text{Etu}^*$	49.60	50.40	1:2	0.42	0.84
5	$\text{AuEtu}_2^+ + 2\text{Etu}^*$	50.17	49.83	1:2	0.34	0.85	

complex in the range of 2–5 *M* or 3–5 *M* salt concentration; a structure cannot be proposed for this complex because the number of trifluoroacetate anions involved in complexation is unknown. The more localized negative charge may be the cause of the higher co-ordinating power of this anion. Only with gold(I) is the 1:2 complex formed in the presence of trifluoroacetate in concentrations from 0.5 to 5.0 *M*; this agrees with the expected greater affinity of this cation for sulphur than for oxygen.

The halide ions exhibit somewhat different behaviour towards the three monovalent cations. With copper(I), only the 1:1 complex is formed with either chloride or bromide. It is difficult to decide whether this complex has a neutral linear structure [CuEtuX], a simple anionic structure [CuEtuX<sub>2</sub>]<sup>-</sup> or a more complicated anionic structure; the fact that this complex has an appreciable *R<sub>F</sub>* value (which is almost constant for the bromides over the whole range of sodium halide concentrations studied) suggests that a stable anionic structure is likely.

A similar 1:1 complex, with an almost constant *R<sub>F</sub>* value over the whole range of sodium salt concentrations, is formed with silver(I) chloride. The close *R<sub>F</sub>* values for the copper(I) and silver(I) halides suggests a similar structure for these 1:1 complexes.

In the silver(I) bromide systems, the migrating complex does not have a simple and stable ratio of metal to Etu independent of the initial ratio and of the sodium bromide concentration. The observed ratio of Etu to metal always exceeds 1 and increases with increasing ratio of Etu to metal in the migrating solution. This indicates that the competitive action of Etu towards bromide ions is much higher than that towards chloride ions and that complicated equilibria occur in the migrating solution depending on the initial ratio of Etu to metal and on the sodium halide concentration;

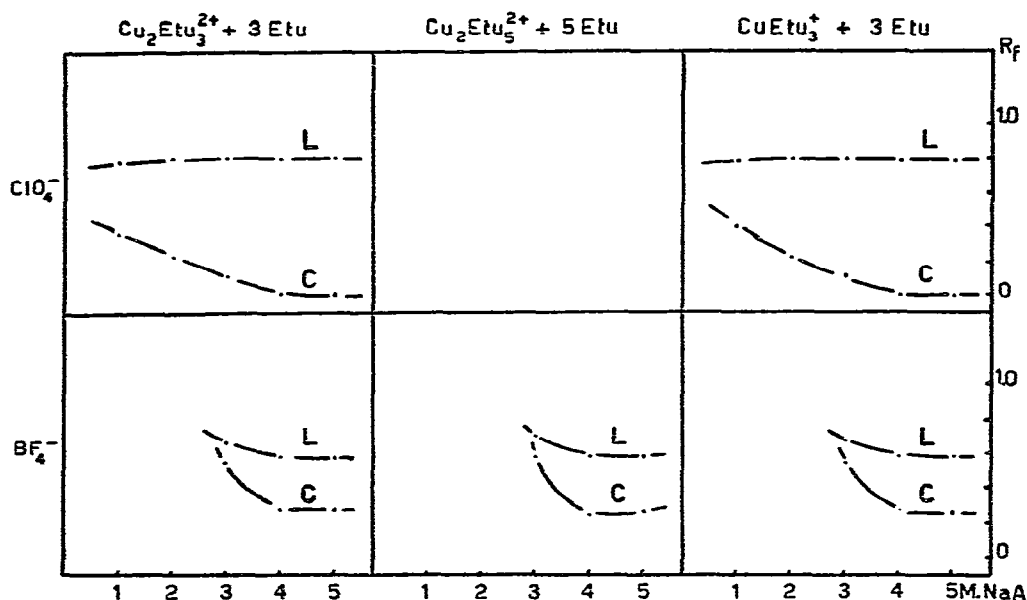


Fig. 1. Variation in *R<sub>F</sub>* for ethylthiourea (Etu = L) and the copper(I)-ethylthiourea complexes (C) with the molarity of NaA (A = ClO<sub>4</sub><sup>-</sup>, BF<sub>4</sub><sup>-</sup>) in the aqueous developing solvent.

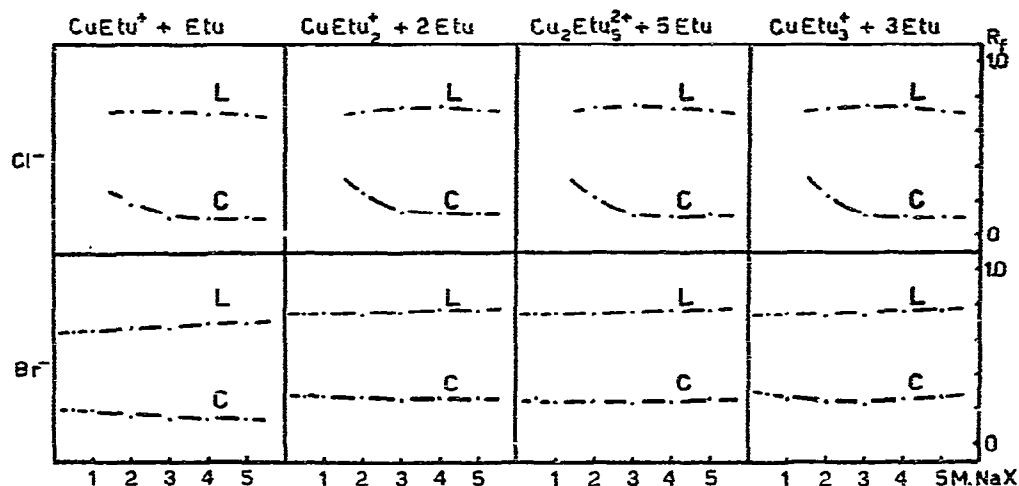


Fig. 2. Variation in  $R_F$  for ethylthiourea ( $\text{Etu} = \text{L}$ ) and copper(I)-ethylthiourea halogen complexes ( $\text{C}$ ) with the molarity of  $\text{NaX}$  ( $\text{X} = \text{Cl}, \text{Br}$ ) in the aqueous eluting solutions.

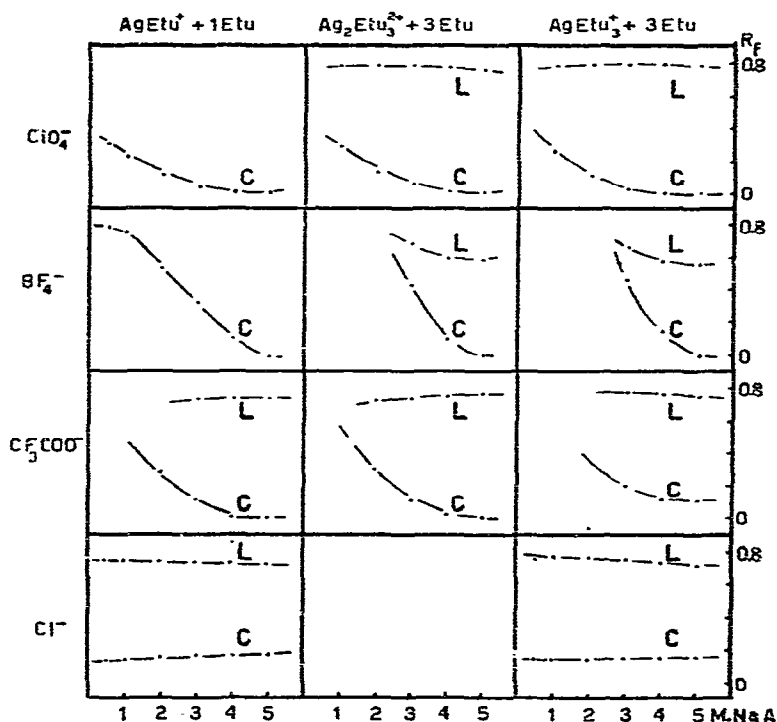


Fig. 3. Variation in  $R_F$  for ethylthiourea ( $\text{Etu} = \text{L}$ ) and silver(I)-ethylthiourea complexes ( $\text{C}$ ) with the molarity of  $\text{NaA}$  ( $\text{A} = \text{ClO}_4, \text{BF}_4, \text{CF}_3\text{COO}, \text{Cl}$ ) in the aqueous developing solvent.



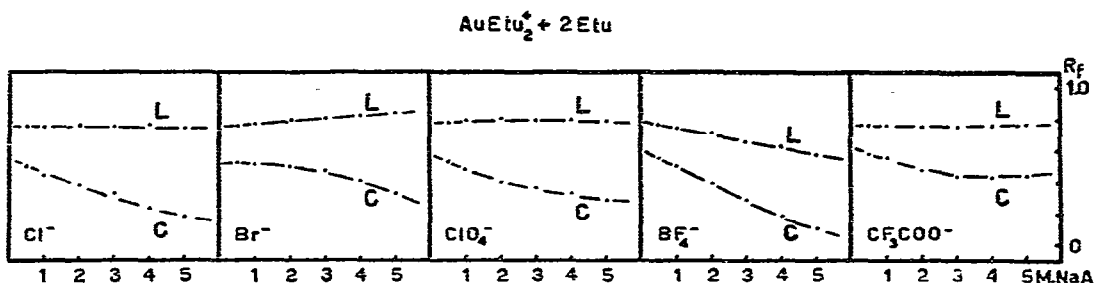


Fig. 4. Variation in  $R_F$  for ethylthiourea ( $\text{Etu} = \text{L}$ ) and  $\text{AuEtu}_2^+$  complexes ( $\text{C}$ ) with the molarity of  $\text{NaA}$  ( $\text{A} = \text{Cl}, \text{Br}, \text{ClO}_4, \text{BF}_4, \text{CF}_3\text{COO}$ ) in the aqueous developing solvent.

consequently, no separation occurs in the sodium bromide concentration range 2–5  $M$ .

With gold(I) systems, only the 1:2 complex is formed, irrespective of the initial ratio of metal to  $\text{Etu}$  and of the sodium halide concentration; this is consistent with the very high affinity of gold(I) for sulphur in comparison with chloride or bromide ions.

The  $R_F$  values of  $\text{Etu}$  (see Tables I–III and Figs. 1–4) are generally almost constant for systems containing perchlorate, trifluoroacetate, chloride or bromide ions, with a slight tendency to increase with the concentration of the sodium salt.

In all the systems investigated, the tetrafluoroborate anion tended to depress the  $R_F$  value for free  $\text{Etu}$  with increasing concentration of sodium tetrafluoroborate; the same effect was observed for the palladium(II) and platinum(II) systems<sup>4</sup> with the same developing solutions. This effect may be due to the ability of the tetrafluoroborate ion to form strong hydrogen bonds with water,  $\text{Etu}$  and the hydroxy-groups of the cellulose of the paper, and thereby diminish free migration of  $\text{Etu}$  on the paper.

The  $R_F$  values of the complexes in most of the systems investigated decrease rapidly with increasing concentration of the sodium salt in the developing solvent. This decrease is particularly sharp for the copper(I) and silver(I) complexes in tetrafluoroborate and trifluoroacetate systems. For these complexes, the  $R_F$  values in chloride and bromide systems are much less sensitive to the sodium concentration than to those of the other anions.

For the gold(I) complexes, there is a general tendency for the  $R_F$  value to decrease with increasing sodium salt concentration. This behaviour suggests that, besides the increasing salting-out effect, other factors may influence the variation in  $R_F$  with increasing sodium salt concentration, e.g., the ability of the anion to form stronger or weaker hydrogen bonds, the chemical constitution and the steric structure of the migrating complex.

For some copper(I) and silver(I) perchlorate, fluoroborate and trifluoroacetate systems, the  $R_F$  value of the migrating complex, in the less concentrated sodium salt solutions, is very close (or equal) to that of the free migrating  $\text{Etu}$ , so that no separation could be observed. For copper(I), the maximum sodium salt concentration at which no separation occurs is:  $\text{ClO}_4^- = 0.5 M$ ,  $\text{BF}_4^- = 2 M$ ,  $\text{CF}_3\text{COO}^- = 5 M$ ; for silver(I) complexes:  $\text{ClO}_4^- = 0.5 M$ ,  $\text{BF}_4^- = 2 M$ ,  $\text{CF}_3\text{COO}^- = 2 M$ .

A comparison of the ratios of  $\text{Etu}$  to metal (Table IV) observed in the solid complexes, by conductometric and high-frequency titration in 2-methoxyethanol or dimethylformamide and by paper radiochromatography shows that, in some instances,

TABLE IV  
OBSERVED RATIOS OF ETHYLTHIOUREA (Etu) TO METAL

Anion (A)	In the solid complexes			By high-frequency and conductometric titrations						By paper chromatography							
	Cu	Ag	Au	Cu	Ag	Au	Cu	Ag	Au	Cu	Ag	Au					
Cl <sup>-</sup>	1	2	2.5	3	1	—	3	2	2	2.5	3*	—	2	3*	1	1	2
Br <sup>-</sup>	1	2	2.5	3	1	—	3	2	2	2.5	3*	—	2	3*	1	—	2
I <sup>-</sup>	1	1.5	—	3	—	—	3	2	1.5	2	3*	—	2	—	—	—	—
ClO <sub>4</sub> <sup>-</sup>	—	1.5	—	3	1	1.5	2	3	—	—	—	—	—	1.5	2	3**	2
BF <sub>4</sub> <sup>-</sup>	—	1.5	—	2.5	3	1	1.5	2	2	—	—	—	—	1.5	2	3**	2
CF <sub>3</sub> COO <sup>-</sup>	—	1.5	—	3	1	1.5	—	3	—	—	—	—	—	1.5	2	3**	2

\* In acidic dimethylformamide solution of CuEtuA (A = Cl, Br, I) and AgEtuA (A = Cl, Br).

\*\* In acidic 2-methoxyethanol solution of AgEtuA (A = ClO<sub>4</sub>, BF<sub>4</sub>, CF<sub>3</sub>COO).

the radiochromatographic method has revealed complexes not identified by the other methods. The complexes migrating in compact spots on paper are highly stable in these developing solvents.

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