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RADIOCHROMATOGRAPHIC AND HIGH-FREQUENCY TITRATION STUDIES ON ETHYLTHIOUREA COMPLEXES OF PALLADIUM(II) AND PLATINUM(II)

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SUMMARY

Some solid palladium(II) and platinum(II) complexes of ethylthiourea (Etu) were prepared. Those with stoichiometry $M(Etu)_4A_2$ ($A=ClO_4$, BF_4, CF_3COO) and $M(Etu)_4X_2$ ($X=Cl$, Br, I) behave in solution as 1:2 electrolytes; the complexes $MEtuX_2$ ($X=Cl$, Br, I) are non-electrolytes, presumably with a dimeric halogen-bridged structure. High-frequency titrations indicated the formation of halide complexes with a ratio of Etu:M of 1:1, 2:1 and 4:1 in acidic, aqueous and dimethylformamide (DMF) solutions, respectively; Pd gives also the 3:1 complexes in DMF. By paper chromatographic elution of mixtures of the complexes and ^{35}S-labelled ethylthiourea with aqueous solutions (0.5–5.0 *M*) of the corresponding NaA or NaX salts, the migrating species $M(Etu^*)_4X_2$ and $M(Etu^*)_4A_2$ were observed. In the case of the chlorides and bromides, two complex species migrating on the chromatographic paper in compact and distinct spots were observed: one with an R_F value almost equal to that of the $M(Etu^*)_4^{2+}$ species, the other with a much lower R_F value. With increasing NaX concentrations of the eluting solution, the first complex decreases until it disappears and the second increases up to 100% for solutions 4–5 *M* in NaX. The second species can be considered as a square pyramidal five-coordinated complex, $[ML_4X]^+$.

INTRODUCTION

In previous studies[1-3] we demonstrated the possibility of the quantitative determination of the composition of metal–thiourea complexes migrating in compact and distinct spots by a paper radiochromatographic method using ^{35}S-labelled thiourea. The thiourea complexes of zinc(II), cadmium(II) and mercury(II)[1], copper(I), silver(I) and gold(I)[2] and palladium(II) and platinum(II)[3] were investigated by this method. We have now extended these investigations to the palladium(II) and platinum(II) complexes of ethylthiourea (Etu) by preparing the solid complexes containing complexing (Cl^-, Br^-, I^-) or non-complexing (ClO_4^-, BF_4^-, CF_3COO^-) anions, studying their stability on paper chromatographic elution and their composition in solution by high-frequency titration.

EXPERIMENTAL

Preparation of the solid complexes

$Pd(Etu)_4A_2$ ($A=ClO_4$, BF_4, CF_3COO). Palladium(II) hydroxide (2 mmole), freshly prepared from palladium(II) nitrate dihydrate by precipitation with potassium hydrogen carbonate and carefully washed by centrifugation, was dissolved in 10 ml of an aqueous solution of 8 mmole of Etu and 4 mmole of perchloric, fluoboric or trifluoroacetic acid. The solution, concentrated *in vacuo*, gave a red oil. In the case of perchlorate, the oil was dissolved in acetone giving, on cooling to 5°, a crystalline product. In the other cases, the oil was dissolved in methanol and the solution evaporated under vacuum over potassium hydroxide. The residue of the trifluoroacetate was microcrystalline; that of the fluoborate was obtained in a crystalline form after dissolving it several times in diethyl ether and evaporating the solution to dryness over potassium hydroxide.

$PdEtuX_2$ ($X=Cl$, Br). Palladium(II) oxide (3 mmole) was dissolved in 10 ml of concentrated hydrochloric acid (37%) or concentrated hydrobromic acid (48%) and the filtered solution was diluted to a 4 *M* HX concentration; then a solution of 3 m*M* Etu in 10 ml of water was added. The precipitate was filtered after 12 h at 5° and washed with ice–water, methanol and diethyl ether, and dried.

$Pd(Etu)_4X_2$ ($X=Cl$, Br, I). For the chloride, 8 mmole of solid Etu were dissolved in a solution of 2 mmole of palladium(II) chloride in 20 ml of water acidified with hydrochloric acid; the red-brown precipitate became orange-yellow on stirring. For the bromide and iodide, 2 mmole of freshly prepared palladium(II) hydroxide were dissolved in 10 ml of an aqueous solution of 8 mmole of Etu containing 4 mmole of hydrobromic or hydriodic acid. In the case of bromide, the solution was then evaporated to dryness under vacuum and the crystalline residue was recrystallized from methanol. In the case of the iodide, the evaporation gave an oil which was repeatedly dissolved in methylene chloride and the solution evaporated under vacuum to dryness until a crystalline product was obtained.

$Pt(Etu)_4A_2$ ($A=ClO_4$, BF_4, CF_3COO). In the case of the perchlorate and fluoborate, 1 mmole of solid platinum(II) chloride was dissolved in small portions by stirring in a warm solution of 4 mmole of Etu in 10 ml of 14% perchloric acid or 5 ml of 31% fluoboric acid. By cooling for several days at 5°, a crystalline product was obtained. In the case of the fluoroacetate, a solution of $Pt(Etu)_4(ClO_4)_2$ in 5 ml of ethanol was added to a solution of 1 mmole of potassium trifluoroacetate in 3 ml of ethanol. The precipitate of potassium chlorate was filtered and the solution evaporated to dryness. The residue was recrystallized from 2 ml of warm water by cooling.

$PtEtuX_2$ ($X=Cl$, Br, I). For the chloride and bromide, a solution of 0.7 mmole of Etu in 3 ml of water was added drop by drop with stirring to a warm solution of 0.7 mmole of potassium tetrachloroplatinate(II) in 7 ml of 4 *M* hydrochloric or hydrobromic acid. The precipitate was filtered after several hours and washed with water, ethanol and diethyl ether and dried under vacuum over potassium hydroxide. In the case of the iodide, a solution of 0.8 mmole of Etu in 3 ml of water was added drop by drop with stirring to a solution of 0.8 mmole of potassium tetrachloroplatinate(II) in 10 ml of 23% hydriodic acid. The compound precipitated immediately.

$Pt(Etu)_4X_2$ (X=Cl, Br, I). The chloride was prepared by adding a warm solution of 0.5 mmole of potassium tetrachloroplatinate(II) in 3 ml of water to a warm solution of 2 mmole of Etu in 5 ml of water and cooling; the other two complexes were prepared by dissolving 0.5 mmole of solid platinum(II) bromide or iodide in small portions in a warm solution of 2 mmole of Etu in 3 ml of water. The solution of the bromide was then concentrated to half its volume; the compound was crystallized by cooling at 5° for several hours. The solution of the iodide, concentrated under vacuum, gave a dark yellow oil, which was dissolved in a few drops of 95% ethanol, giving a crystalline product by standing the solution at 5° for several hours. It was not possible to obtain solid complexes with M:Etu ratios of 1:2 or 1:3. The compounds were analysed by standard methods (Table I).

Paper chromatography and radiochromatography

Several systems were investigated by the ascending method on 35 × 1 cm strips of Whatman No. 1 paper at room temperature, using for the elution an aqueous solution of the sodium salt containing the same anion as the investigated complex, with the concentrations indicated in Tables IV and V.

Preliminary experiments showed that with these eluting solutions, both the ethylthiourea and the complexes migrated on the paper strip in compact and separate spots. Ethylthiourea was identified on the strips, after elution and drying, with a 0.05 *M* aqueous solution of iodine containing potassium iodide or with the Roche[4] reagent (one volume each of 10% sodium hydroxide, 10% sodium nitroprussiate, 10% potassium hexacyanoferrate(III) and three volumes of water). The metal ion of the complex was identified on the strip with a 0.2% ethanolic solution of rubeanic acid, which gives a red-brown colour with palladium(II) and a red colour with platinum(II).

Other experiments have shown that in solution ^{35}S-labelled ethylthiourea instantaneously and completely exchanges with the inactive ethylthiourea bonded to the metal ion in the complex, so that the kinetics of this exchange cannot be studied. This fact, however, can be used to determine the composition of the complexes migrating on the paper strip.

For the radiochromatographic experiments, a 0.1 *M* aqueous solution of ^{35}S-labelled ethylthiourea and an aqueous solution of the Etu complex 0.1 *M* in complexed ethylthiourea were mixed in order to give the Etu:Etu* ratios indicated in Tables IV and V. Normally, 10 μl of these mixtures were used for each radiochromatographic experiment. After elution and drying, the strips were scanned with a Geiger-Müller counter measuring the radioactivity of successive areas of 1 × 1 cm. All the radioactivity present in the starting spot was recovered in the two or three spots indicated in Tables IV and V.

High-frequency titrations and conductivity measurements

High-frequency (H.F.) titrations were carried out with a WTW titrimeter, Type HFT 3C, working at a frequency of 30 MHz (± 1 %), using the deflection method and a 10-ml semi-micro cell made of titanium ceramic. Solutions ($2 \cdot 10^{-3}$ *M*) of K_2PdX_4 (X=Cl, Br) and K_2PtX_4 (X=Cl, Br, I) in aqueous HX ($2 \cdot 10^{-3}$ *M*), in order to avoid hydrolysis, and solutions of $PdEtuX_2$ (X=Cl, Br) or $PtEtuX_2$ (X=Cl, Br, I) in dimethylformamide (DMF) were titrated with an $8 \cdot 10^{-2}$ *M* aqueous or DMF solution of ethylthiourea. In all instances straight lines were obtained, intersecting each other at the Etu:M ratios indicated in Table II.

Conductivities were measured with a WTW, LBR-type conductivity bridge on 10^{-3} *M* solutions of the complexes in methanol or DMF and on 10^{-3} *M* solutions of the complexes in an $8 \cdot 10^{-2}$ *M* solution of thiourea in the same solvents (Table III).

RESULTS AND DISCUSSION

All the solid complexes of ethylthiourea with palladium(II) and platinum(II) (Tables I and II) containing either coordinating or non-coordinating anions show a maximum ethylthiourea:metal ratio of 4:1, independent of the anion used. This indicates that the 4:1 ethylthiourea:metal ratio used in the preparation of these complexes is, in all instances, sufficient to ensure the coordination of four molecules of ethylthiourea and that the competitive action of halide ions towards the ethylthiourea coordination is virtually absent even in the presence of an excess of free hydrochloric acid as in the case of the preparation of $Pd(Etu)_4Cl_2$. The 4:1 complexes obviously have a square planar 4S-coordination.

TABLE I

COLOUR, YIELD AND ANALYTICAL RESULTS FOR VARIOUS COMPLEXES

Results for analyses are given as values found and values calculated (in parentheses).

Compound	*Colour*	*Yield (%)*	*M (%)*	*S (%)*	*N (%)*
$PdEtuCl_2$	orange-red	95	37.72 (37.80)	11.24 (11.39)	10.04 (9.94)
$PdEtu_4Cl_2$	gold-yellow	90	18.06 (17.91)	21.40 (21.59)	18.76 (18.86)
$PdEtuBr_2$	red-brown	88	28.63 (28.72)	8.53 (8.65)	7.49 (7.55)
$PdEtu_4Br_2$	orange-brown	94	15.58 (15.58)	18.63 (18.78)	16.36 (16.40)
$PdEtu_4I_2$	red-brown	96	13.32 (13.69)	16.49 (16.72)	14.32 (14.42)
$PdEtu_4(ClO_4)_2$	red-orange	76	14.82 (14.74)	17.61 (17.76)	15.48 (15.51)
$PdEtu_4(BF_4)_2$	red-brown	68	15.33 (15.27)	18.42 (18.40)	16.20 (16.07)
$PdEtu_4(CF_3COO)_2 \cdot CF_3COOH$	gold-yellow	84	12.41 (12.32)	14.59 (14.85)	12.97 (12.97)
$PtEtuCl_2$	orange-yellow	95	52.53 (52.70)	8.52 (8.66)	
$PtEtu_4Cl_2$	yellow	91	28.55 (28.57)	18.64 (18.78)	
$PtEtuBr_2$	orange	95	42.36 (42.49)	6.72 (6.98)	
$PtEtu_4Br_2$	sulphur yellow	92	25.22 (25.28)	16.48 (16.61)	
$PtEtuI_2$	dark brown	96	35.39 (35.27)	5.60 (5.79)	
$PtEtu_4I_2$	yellow	91	22.51 (22.53)	14.70 (14.81)	
$PtEtu_4(ClO_4)_2$	lemon yellow	90	24.03 (24.06)	15.72 (15.81)	
$PtEtu_4(BF_4)_2$	yellow	70	24.86 (24.83)	16.08 (16.32)	
$PtEtu_4(CF_3COO)_2 \cdot 2\,H_2O$	lemon yellow	78	22.28 (22.32)	14.52 (14.67)	

Of the other possible ethylthiourea:metal ratios, only the 1:1 complexes, $MEtuX_2$ (X=Cl, Br, I), could be obtained in the solid state. These correspond to the general stoichiometry of unidentate ligand–dihalide complexes of these metals, having a square planar binuclear halogen-bridged coordination, $[MLX_2]_2$. The fact that other halide complexes with intermediate ethylthiourea:metal ratios were not obtained in the solid state, while thiourea gives solid 2:1 complexes with both metals[3], may be

TABLE II

OBSERVED ETHYLTHIOUREA:METAL RATIOS

Anion, A	*In the solid complexes*		*By H.F. titration*				*By paper chromatography*§§	
	Pd	*Pt*	*Pd**	*Pt***	*Pd****	*Pt*§	*Pd*	*Pt*
Cl^-	1 4	1 4	1 2 4	1 2 4	1 2 3 4	1 2 4	4	4
Br^-	1 4	1 4	1 2 4	1 2 4	1 2 3 4	1 2 4	4	4
I^-	— 4	1 4	— — —	1 2 4	— — — —	1 2 4	4	4
ClO_4^-	— 4	— 4					4	4
BF_4^-	— 4	— 4					4	4
CF_3COO^-	— 4	— 4					4	4

* In acidic aqueous solution of K_2PdX_4 (X=Cl,Br).

** In acidic aqueous solution of K_2PtX_4 (X=Cl,Br,I).

*** In DMF solution of $PdEtuX_2$ (X=Cl,Br).

§ In DMF solution of $PtEtuX_2$ (X=Cl,Br,I).

§§ With aqueous solutions of the sodium salt (0.5–5.0 *M*).

due to the influence of the greater steric hindrance of the ethylthiourea in the crystallization process.

The molar conductivities (Table III) indicate that only in the case of $Pd(Etu)_4I_2$ does an excess of ethylthiourea of about 80 times that of the complex significantly increase the conductivity of the complex solution in both solvents (112

TABLE III

MOLAR CONDUCTIVITIES ($\Omega^{-1}\cdot cm^2\cdot mole^{-1}$) OF THE COMPLEXES $MEtuX_2$, $M(Etu)_4X_2$ AND $M(Etu)_4A_2$

Concentrations $1\cdot10^{-3}$ *M*; temperature 25 °C.

Complex	*MeOH*	*MeOH + 8·10⁻² M Etu*	*DMF*	*DMF + 8·10⁻² M Etu*
$PdEtu_4Cl_2$	105	108	37	45
$PdEtu_4Br_2$	117	121	61	64
$PdEtu_4I_2$	112	137	64	106
$PdEtu_4(CF_3COO)_2$	133	133	71	76
$PdEtu_4(BF_4)_2$	167	163	138	134
$PdEtu_4(ClO_4)_2$	169	162	134	130
$[PdEtuCl_2]_2$	Insoluble	—	7	—
$[PdEtuBr_2]_2$	Insoluble	—	9	—
$PtEtu_4Cl_2$	119	119	48	46
$PtEtu_4Br_2$	128	122	68	62
$PtEtu_4I_2$	143	143	101	116
$PtEtu_4(CF_3COO)_2\cdot 2\,H_2O$	137	134	83	83
$PtEtu_4(BF_4)_2$	174	171	144	140
$PtEtu_4(ClO_4)_2$	174	171	135	135
$[PtEtuCl_2]_2$	Insoluble	—	6	—
$[PtEtuBr_2]_2$	Insoluble	—	6	—
$[PtEtuI_2]_2$	Insoluble	—	7	—

to 137 in methanol, 64 to 106 in DMF). This effect is less evident for palladium(II) chloride and bromide and may be due to a substitution mechanism either in the square planar coordination:

$$[PdEtu_3X]^+ + Etu \rightleftharpoons [PdEtu_4]^{2+} + X^-$$

or in a square pyramidal five-coordination of the metal:

$$[PdEtu_4X]^+ + Etu \rightleftharpoons [PdEtu_5]^{2+} + X^-$$

The last mechanism seems to be preferable owing to the tendency of palladium(II) to assume a five-coordination, and considering that a Etu:Pd ratio of 4:1 in the presence of a large excess of halide ions always gives the solid compound $PdEtu_4X_2$ and never the complex $PdEtu_3X_2$.

The increase in the conductivity from the chloride to the iodide, in the presence of the same excess of the ligand, may indicate that electrostatic interactions occur between the $[MEtu_4]^{2+}$ ion and these anions, decreasing in the order $Cl^- > Br^- > I^-$. The conductivity of the $M(Etu)_4(CF_3COO)_2$ complexes, which are much lower than those of the corresponding perchlorates and fluoborates, may indicate that the trifluoroacetate ion has an electrostatic action comparable with that of the iodide for the platinum complexes; in this case, the decrease in conductivity may also be attributed to hydrogen bonds between the NH groups of the ethylthiourea and the anion.

The very low conductivities of the $MEtuX_2$ complexes show that these compounds are non-electrolytes with a dimeric halogen-bridged structure.

The high-frequency titrations indicate that in aqueous acidic solution the 1:1, 2:1, and 4:1 complexes are formed, while in DMF solution the 1:1, 2:1, 3:1 and 4:1 complexes for palladium(II) and 1:1, 2:1, 4:1 complexes for platinum(II) can exist. The existence of a 3:1 palladium(II) complex in DMF was also observed for thiourea, and in both instances it may correspond either to a partially ionic square planar structure, $[PdL_3X]X$, or to a neutral pentacoordinated complex, $[PdL_3X_2]$, in agreement with the greater tendency of palladium(II) to assume a square pyramidal pentacoordination than that of platinum(II)[3]. The occurrence of this 3:1 complex in the less ionizing DMF seems to indicate that the non-ionic pentacoordinate form is the most likely.

In solution, the coordinated ethylthiourea in the Pd(II) and Pt(II) complexes instantaneously exchanges with free ^{35}S-labelled ethylthiourea (Etu*). By eluting a mixture of 1 *M* $EtuX_2$ (M=Pd, Pt; X=Cl, Br, I) plus 1 *M* Etu* with a solution of the corresponding NaX salt from 0.5 to 5.0 *M* concentrations, a dispersion of both the metal ion and the ethylthiourea along the paper strip was obtained. Only the $M(Etu)_4^{2+}$ species was found to be stable on elution under these conditions. In Tables IV and V are reported the results of the experiments performed with mixtures $MEtuX_2$ (X=Cl, Br) plus 3 Etu* and $M(Etu)_4A_2$ ($A=ClO_4$, BF_4, CF_3COO) or $M(Etu)_4X_2$ (X=Cl, Br) plus 4 Etu* by eluting them with aqueous solutions of the corresponding NaA or NaX salt from 0.5 to 5.0 *M* concentrations.

Except for a few instances in which no separation occurs, the composition of the complex species migrating in a compact spot is always $M(Etu^*)_4^{2+}$, with R_F values

TABLE IV

PAPER CHROMATOGRAPHY OF Pd(II) COMPLEXES WITH ETHYLTHIOUREA (Etu) ADDED WITH FREE ^{35}S-ETHYLTHIOUREA (Etu*) IN AQUEOUS 0.5–5.0 *M* SOLUTIONS OF THE SODIUM SALT (NaA)

Temperature 20 °C.

Anion, A	*Aqueous solution of NaA (M)*	*Eluted substance*	*Etu* complexed (%)*	*Etu* free (%)*	*Pd:Etu*	R_F	
						Complex	*Etu*
ClO_4^-	0.5	$Etu_4Pd^{2+} + 4Etu^*$	49.7	50.3	1:4	0.62	0.76
	1	$Etu_4Pd^{2+} + 4Etu^*$	50.1	49.9	1:4	0.60	0.78
	2	$Etu_4Pd^{2+} + 4Etu^*$	50.2	49.8	1:4	0.58	0.80
	3	$Etu_4Pd^{2+} + 4Etu^*$	49.7	50.3	1:4	0.50	0.80
	4	$Etu_4Pd^{2+} + 4Etu^*$	49.5	50.5	1:4	0.40	0.80
	5	$Etu_4Pd^{2+} + 4Etu^*$	50.2	49.8	1:4	0.33	0.78
BF_4^-	0.5	$Etu_4Pd^{2+} + 4Etu^*$	No separation				
	1	$Etu_4Pd^{2+} + 4Etu^*$	No separation				
	2	$Etu_4Pd^{2+} + 4Etu^*$	50.0	50.0	1:4	0.60	0.73
	3	$Etu_4Pd^{2+} + 4Etu^*$	49.8	50.2	1:4	0.45	0.69
	4	$Etu_4Pd^{2+} + 4Etu^*$	50.2	49.8	1:4	0.31	0.63
	5	$Etu_4Pd^{2+} + 4Etu^*$	50.6	49.4	1:4	0.16	0.53
CF_3COO^-	0.5	$Etu_4Pd^{2+} + 4Etu^*$	No separation				
	1	$Etu_4Pd^{2+} + 4Etu^*$	No separation				
	2	$Etu_4Pd^{2+} + 4Etu^*$	No separation				
	3	$Etu_4Pd^{2+} + 4Etu^*$	No separation				
	4	$Etu_4Pd^{2+} + 4Etu^*$	No separation				
	5	$Etu_4Pd^{2+} + 4Etu^*$	No separation				
Cl^-	0.5	$EtuPd^{2+} + 3Etu^*$	100		1:4	0.67	
	1	$EtuPd^{2+} + 3Etu^*$	100		1:4	0.66	
	2	$EtuPd^{2+} + 3Etu^*$	88.4 11.6			0.58 0.12	
	3	$EtuPd^{2+} + 3Etu^*$	56.3 46.7			0.48 0.09	
	4	$EtuPd^{2+} + 3Etu^*$	100		1:4	0.00	
	5	$EtuPd^{2+} + 3Etu^*$	100		1:4	0.00	
	0.5	$Etu_4Pd^{2+} + 4Etu^*$	50.3	49.7	1:4	0.69	0.78
	1	$Etu_4Pd^{2+} + 4Etu^*$	49.9	50.1	1:4	0.66	0.77
	2	$Etu_4Pd^{2+} + 4Etu^*$	6.4 42.9	50.7		0.58 0.16	0.76
	3	$Etu_4Pd^{2+} + 4Etu^*$	49.6	50.4	1:4	0.07	0.77
	4	$Etu_4Pd^{2+} + 4Etu^*$	49.4	50.6	1:4	0.00	0.75
	5	$Etu_4Pd^{2+} + 4Etu^*$	50.3	49.7	1:4	0.00	0.76
Br^-	0.5	$EtuPd^{2+} + 3Etu^*$	100		1:4	0.64	
	1	$EtuPd^{2+} + 3Etu^*$	100		1:4	0.63	
	2	$EtuPd^{2+} + 3Etu^*$	100		1:4	0.60	
	3	$EtuPd^{2+} + 3Etu^*$	26.4 73.6			0.60 0.15	
	4	$EtuPd^{2+} + 3Etu^*$	100		1:4	0.04	
	5	$EtuPd^{2+} + 3Etu^*$	100		1:4	0.00	
	0.5	$Etu_4Pd^{2+} + 4Etu^*$	50.1	49.9	1:4	0.65	0.77
	1	$Etu_4Pd^{2+} + 4Etu^*$	49.7	50.3	1:4	0.64	0.79
	2	$Etu_4Pd^{2+} + 4Etu^*$	50.4	49.6	1:4	0.62	0.80
	3	$Etu_4Pd^{2+} + 4Etu^*$	49.7	50.3	1:4	0.61	0.82
	4	$Etu_4Pd^{2+} + 4Etu^*$	13.5 36.8	49.7		0.60 0.11	0.84
	5	$Etu_4Pd^{2+} + 4Etu^*$	49.9	50.1	1:4	0.08	0.88

TABLE V

PAPER CHROMATOGRAPHY OF Pt(II) COMPLEXES WITH ETHYLTHIOUREA (Etu) ADDED WITH FREE ^{35}S-ETHYLTHIOUREA (Etu*) IN AQUEOUS 0.5–5.0 *M* SOLUTIONS OF THE SODIUM SALT (NaA)

Temperature 20 °C.

Anion, A	*Aqueous solution of NaA (M)*	*Eluted substance*	*Etu* complexed (%)*	*Etu* free (%)*	*Pt:Etu*	R_F	
						Complex	*Etu*
ClO_4^-	0.5	$Etu_4Pt^{2+} + 4Etu^*$	49.9	50.1	1:4	0.61	0.75
	1	$Etu_4Pt^{2+} + 4Etu^*$	50.4	49.6	1:4	0.59	0.77
	2	$Etu_4Pt^{2+} + 4Etu^*$	49.9	50.1	1:4	0.56	0.80
	3	$Etu_4Pt^{2+} + 4Etu^*$	49.8	50.2	1:4	0.52	0.80
	4	$Etu_4Pt^{2+} + 4Etu^*$	50.1	49.9	1:4	0.41	0.80
	5	$Etu_4Pt^{2+} + 4Etu^*$	50.2	49.8	1:4	0.23	0.79
BF_4^-	0.5	$Etu_4Pt^{2+} + 4Etu^*$	No separation				
	1	$Etu_4Pt^{2+} + 4Etu^*$	No separation				
	2	$Etu_4Pt^{2+} + 4Etu^*$	50.7	49.3	1:4	0.55	0.70
	3	$Etu_4Pt^{2+} + 4Etu^*$	50.4	49.6	1:4	0.43	0.66
	4	$Etu_4Pt^{2+} + 4Etu^*$	49.8	50.2	1:4	0.26	0.63
	5	$Etu_4Pt^{2+} + 4Etu^*$	49.7	50.3	1:4	0.13	0.55
CF_3COO^-	0.5	$Etu_4Pt^{2+} + 4Etu^*$	No separation				
	1	$Etu_4Pt^{2+} + 4Etu^*$	No separation				
	2	$Etu_4Pt^{2+} + 4Etu^*$	50.4	49.6	1:4	0.64	0.75
	3	$Etu_4Pt^{2+} + 4Etu^*$	48.9	51.1	1:4	0.54	0.74
	4	$Etu_4Pt^{2+} + 4Etu^*$	49.9	50.1	1:4	0.51	0.74
	5	$Etu_4Pt^{2+} + 4Etu^*$	50.3	49.7	1:4	0.50	0.75
Cl^-	0.5	$EtuPt^{2+} + 3Etu^*$	92.0 8.0			0.67 0.42	
	1	$EtuPt^{2+} + 3Etu^*$	89.3 10.7			0.64 0.33	
	2	$EtuPt^{2+} + 3Etu^*$	73.4 26.6			0.56 0.18	
	3	$EtuPt^{2+} + 3Etu^*$	57.3 42.7			0.43 0.02	
	4	$EtuPt^{2+} + 3Etu^*$	35.7 64.3			0.34 0.01	
	5	$EtuPt^{2+} + 3Etu^*$	100		1:4	0.00	
	0.5	$Etu_4Pt^{2+} + 4Etu^*$	49.5	50.5	1:4	0.72	0.78
	1	$Etu_4Pt^{2+} + 4Etu^*$	49.2	50.8	1:4	0.64	0.77
	2	$Etu_4Pt^{2+} + 4Etu^*$	48.1 1.2	50.7		0.55 0.15	0.77
	3	$Etu_4Pt^{2+} + 4Etu^*$	41.4 9.6	49.0		0.47 0.03	0.76
	4	$Etu_4Pt^{2+} + 4Etu^*$	4.5 45.8	49.7		0.41 0.02	0.76
	5	$Etu_4Pt^{2+} + 4Etu^*$	50.1	49.9	1:4	0.02	0.74
Br^-	0.5	$EtuPt^{2+} + 3Etu^*$	100		1:4	0.65	
	1	$EtuPt^{2+} + 3Etu^*$	100		1:4	0.64	
	2	$EtuPt^{2+} + 3Etu^*$	100		1:4	0.62	
	3	$EtuPt^{2+} + 3Etu^*$	84.7 15.3			0.50 0.06	
	4	$EtuPt^{2+} + 3Etu^*$	41.4 58.6			0.47 0.03	

TABLE V *(continued)*

Anion, A	*Aqueous solution of NaA (M)*	*Eluted substance*	*Etu* complexed (%)*	*Etu* free (%)*	*Pt:Etu*	*R_F*	
						Complex	*Etu*
	5	EtuPt^{2+} + 3Etu*	14.9 85.1			0.47 0.02	
	0.5	Etu$_4$Pt^{2+} + 4Etu*	49.9	50.1	1:4	0.63	0.76
	1	Etu$_4$Pt^{2+} + 4Etu*	49.9	50.1	1:4	0.62	0.78
	2	Etu$_4$Pt^{2+} + 4Etu*	49.7	50.3	1:4	0.61	0.81
	3	Etu$_4$Pt^{2+} + 4Etu*	49.9	50.1	1:4	0.53	0.85
	4	Etu$_4$Pt^{2+} + 4Etu*	36.7 13.4	49.9		0.46 0.09	0.86
	5	Etu$_4$Pt^{2+} + 4Etu*	10.1 40.0	49.9		0.46 0.03	0.86

dependent on several factors that will be considered later. Normally, in the halide systems

$$\mathrm{MEtuX_2 + 3\,Etu^* \rightarrow M(Etu^*)_4X_2}$$

only one spot, corresponding to the complex, and in the systems

$$\mathrm{M(Etu)_4X_2 + 4Etu^* \rightarrow M(Etu^*)_4X_2 + 4Etu^*}$$

only two spots, corresponding to the complex and to the free ethylthiourea, were observed.

In some instances, two spots containing both the metal ion and ethylthiourea and therefore corresponding to two different complexes were observed (Tables IV and V). With increasing molarity of NaX in the solutions used for the elution of the

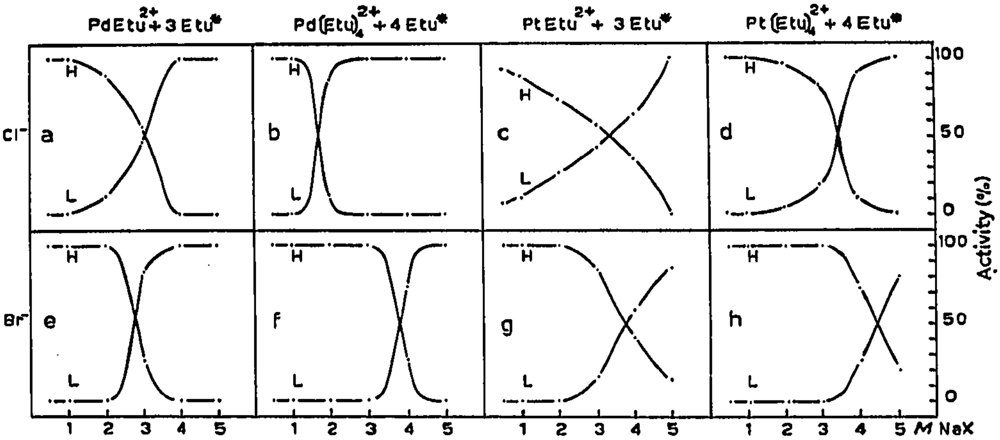


Fig. 1. Increase in the activity of the complexes with high (H) and low (L) R_F values with the molarity of NaX in the aqueous solution for the systems MEtuX$_2$ + 3Etu* and M(Etu)$_4$X$_2$ + 4Etu* (M = Pd, Pt; X = Cl, Br).

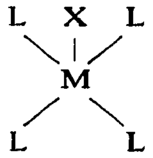
starting mixture, the spot with the highest R_F value decreases both in its activity and in its R_F value, while the spot with the lowest R_F value increases in its activity but decreases in its R_F value (Tables IV and V; Fig. 1). The extent of the percentage variation in activity increases from the chloride to the bromide, from the system $\mathrm{MEtuX_2} + 3\mathrm{Etu}^*$ to the system $\mathrm{M(Etu)_4X_2} + 4\mathrm{Etu}^*$, having an excess of ethylthiourea, and is greater for the Pd(II) than for the Pt(II) complexes. The "equivalence point" of the process, corresponding to 50% of each complex, lies at the NaX molarities of the eluting solution for the different systems shown in Table VI.

TABLE VI

EQUIVALENCE POINTS OF DIFFERENT SYSTEMS

System	*Equivalence point*
$\mathrm{EtuPdCl_2} + 3\mathrm{Etu}^*$	3.1 *M* NaCl
$\mathrm{EtuPdBr_2} + 3\mathrm{Etu}^*$	2.8 *M* NaBr
$\mathrm{Etu_4PdCl_2} + 4\mathrm{Etu}^*$	1.7 *M* NaCl
$\mathrm{Etu_4PdBr_2} + 4\mathrm{Etu}^*$	3.8 *M* NaBr
$\mathrm{EtuPtCl_2} + 3\mathrm{Etu}^*$	3.3 *M* NaCl
$\mathrm{EtuPtBr_2} + 3\mathrm{Etu}^*$	3.8 *M* NaBr
$\mathrm{Etu_4PtCl_2} + 4\mathrm{Etu}^*$	3.5 *M* NaCl
$\mathrm{Etu_4PtBr_2} + 4\mathrm{Etu}^*$	4.4 *M* NaBr

Table VI indicates that the complex with the highest R_F value is more stable for the bromide than for the chloride solution and for platinum(II) than for palladium(II) in both chloride and bromide solutions; the reverse occurs for the complex with the lowest R_F value. The formation of the second complex clearly depends on the concentration of the halide ion in solution and therefore should contain the halide ion in its coordination sphere, very likely in a fifth position:



The strong tendency for palladium(II) to give five-coordinated ions such as $[\mathrm{PdL_4X}]^+$ and $[\mathrm{Pd(NAS)_2X}]^+$ (L=N,N'-diphenylthiourea; NAS=1,8-naphthalenebisdimethylarsine) was demonstrated by conductimetric titrations of the corresponding palladium(II) perchlorate complexes with Cl^- ions in non-polar solvents[5,6]. Platinum(II) shows the same, although weaker, tendency, as demonstrated by the higher values of the NaX molarity at the equivalence point of the platinum(II) complexes.

It is remarkable that the two complexes are formed at the starting spot in relative proportions that depend on the sodium halide concentration in the eluting solution but, after their formation, they migrate in the same solution in compact and separate spots, being no longer in equilibrium with each other.

The R_F values of the complexes $M(Etu)_4A_2$ ($A=ClO_4$, BF_4) (Tables IV and V; Fig. 2a, d) regularly decrease, with increasing NaA molarities, to very low values. As the R_F value of ethylthiourea also decreases in a similar manner in fluoborate solution, the decrease in R_F value in these systems may be attributed to a general salting-out effect and to a lowering of the dissociation of the complexes with the formation of ion pairs. The formation of five-coordinated species with these very weak complexing anions seems to be excluded as no indication of such five-coordination was found, even for the stronger complexing trifluoroacetate anion, for which a lower decrease of the R_F value was observed (Fig. 2e).

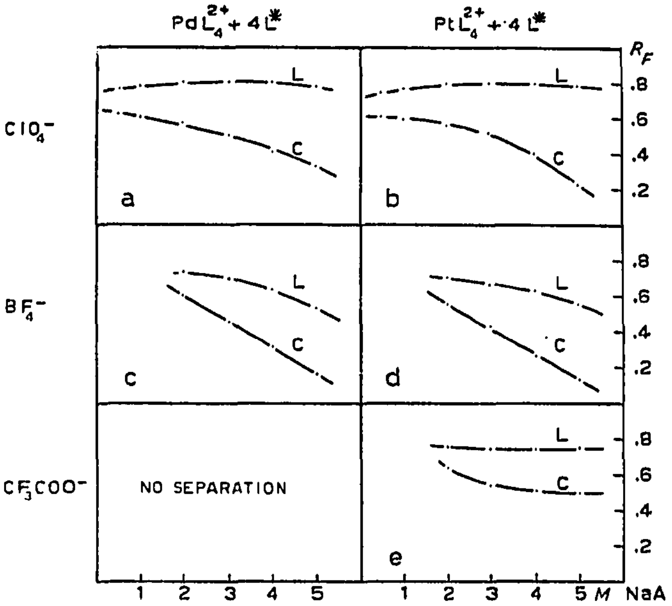


Fig. 2. Variation of the R_F values for the ligand (L) and the complexes (C) PdL_4A_2 (L = Etu; A = ClO_4, BF_4) and PtL_4A_2 (L = Etu; A = ClO_4, BF_4, CF_3COO) with the molarity of NaA in the aqueous eluting solution.

In the systems $M(Etu)_4X_2 + 4Etu^*$ (X=Cl, Br) (Fig. 3b, d, f, h), the effect of the NaA concentration on ethylthiourea is almost negligible, the R_F value of the free ligand being almost constant with chloride concentration and slightly increasing with the increase in bromide concentration in the solution. The rather large decrease in R_F value for both of the complexes may be due to a lowering of the dissociation of the complex salts as a result of the increase in the NaX concentration. This effect is different, however, from the formation of the five-coordinated complex, which has a completely different R_F value.

In the systems $MEtuX_2 + 3Etu^*$ (X = Cl, Br) (Fig. 3a, c, e, g), only two complexes were observed without any free ethylthiourea. The R_F values of these complexes and their variations in the four systems are very similar to those of the two complexes in the four systems containing an excess of ethylthiourea. This is a further demonstra-

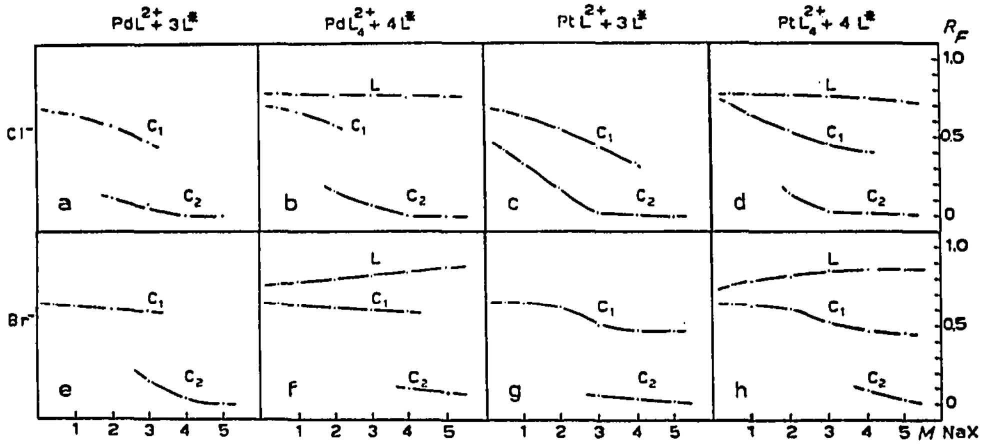


Fig. 3. Variation of the R_F values of the ligand (L) and the complexes $C_1 = [ML_4]X_2$ and $C_2 = M[L_4X]X$ (L = Etu; M = Pd, Pt; X = Cl, Br) with the molarity of NaX in the aqueous eluting solution.

tion that these complexes are the same in the two series of systems, independent of the presence or absence of an excess of free ethylthiourea in the starting solution.

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