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RADIOCHROMATOGRAPHIC, CONDUCTOMETRIC AND HIGH-FREQUENCY TITRATION STUDIES ON THE THIOUREA COMPLEXES OF PALLADIUM(II) AND PLATINUM(II)

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SUMMARY

Palladium(II) and platinum(II) complexes of thiourea, $MTuX_2$, MTu_2X_2 , MTu_4X_2 ($X = Cl, Br, I$) and MTu_4A_2 ($A = ClO_4, BF_4, CF_3COO$), were prepared. Palladium(II) iodide gives a $Pd_3Tu_3I_4Cl_2$ complex. The complexes $PdTuX_2$, $PdTu_2X_2$, $PdTu_4X_2$ ($X = Cl, Br$), $PdTuA_2$, $PdTu_2A_2$, $PdTu_4A_2$ ($A = ClO_4, BF_4, CF_3COO$), $PdTu_3(BF_4)_2$ and $PtTuX_2$, $PtTu_2X_2$, $PtTu_4X_2$ ($X = Cl, Br, I$) were identified by high-frequency titration in aqueous solution. Molar conductivities showed that $MTuX_2$ and MTu_2X_2 are non-electrolytes. In methanol, MTu_4A_2 ($A = ClO_4, BF_4, CF_3COO$) and $PtTu_4X_2$ ($X = Cl, Br, I$) complexes behave as uni-bivalent electrolytes, while $PdTu_4X_2$ ($X = Cl, Br, I$) complexes show a reduced conductivity. The conductivities of the halide and trifluoroacetate complexes are even lower in dimethylformamide and show a partial interaction of the anion with the complex. The elution of the complexes with ketones containing an aqueous solution of the sodium salt and with alcohols containing an aqueous solution of the free acid show that in both cases the only species which migrates in compact spots is the very stable $(MTu_4)^{2+}$ ion, with very high R_F values in the ketone mixture and very low values in the alcohol mixtures.

INTRODUCTION

In previous work, we demonstrated that thiourea complexes of Zn(II), Cd(II) and Hg(II)¹ and of Cu(I), Ag(I) and Au(I)² can be eluted without decomposition and in compact spots on a chromatographic paper strip by using mixtures of a ketone and the aqueous solution of the sodium salt^{1,2} or of an alcohol and the aqueous solution of the free acid². The composition of the migrating complex was determined by radiochemical methods using ³⁵S-labelled thiourea. We have now extended this method of investigation to the thiourea complexes of palladium(II) and platinum(II) in order (a) to compare the behaviour of the halide complexes of these metals with the complexes of their salts containing less coordinating anions, such as perchlorate, fluoborate and trifluoroacetate, (b) to complete systematically the preparation of all the solid complexes, (c) to identify the complexes existing in solution by high-frequency titration, and (d) to study the molar conductivities of the complexes.

EXPERIMENTAL

Preparation of the solid complexes

PdTuCl₂. A solution of thiourea (2 mM) in water (2 ml) was added to a solution of PdCl₂ (2 mM) in 50 ml of aqueous 4 M HCl. The product was washed with water, ethanol and diethyl ether.

PdTuBr₂. PdO (2 mM) was dissolved in 15 ml of 8 M HBr at 70–80° and the solution diluted to 30 ml. When a solution of thiourea (2 mM) in water (2 ml) was added dropwise, the complex immediately precipitated.

Pd₃Tu₃I₄Cl₂. A solution of Na₂PdCl₄ (1 mM) in water (1 ml) was added to a solution of thiourea (1 mM) in 2 ml of water plus 15 ml of 5 M HI. The solution turned deep red, and the product immediately formed was well crystallized and very uniform under the microscope. It was not possible to prepare Na₂PdI₄ as the starting reagent in order to obtain PdTuI₂, nor was the latter complex obtainable by other methods: (a) Solid PdI₂ (1 mM) does not dissolve completely in a solution of thiourea (1 mM) in methylcellosolve and presumably gives in solution a Tu:Pd ratio greater than 1:1. (b) Freshly prepared Pd(OH)₂ (1 mM) was completely dissolved at room temperature in 10 ml of 7.8 M HI and the solution diluted to 15 ml. When solid thiourea (1 mM) was dissolved in this solution no precipitate was formed, and subsequent cooling with ice produced only a small quantity of PdI₂.

PdTu₂X₂ (X = Cl, Br). Solid PdTuX₂ (1 mM) was dissolved at 60–70° in a solution of thiourea (1 mM) in methylcellosolve (40 ml). By evaporating the solvent under vacuum, red-brown oils were obtained. From their concentrated aqueous solutions, microcrystalline products were formed.

PdTu₂I₂. A solution of Na₂PdCl₄ (2 mM) in water (2 ml) was added at room temperature to a solution of thiourea (4 mM) in 20 ml of 5 M HI. The product precipitated immediately and was washed with water and ethanol.

PdTu₄Cl₂. This was prepared by the method of KURNAKOW³ and recrystallized from hot water.

PdTu₄Br₂. A concentrated aqueous solution of thiourea (4 mM) was added to a solution of Na₂PdBr₄ (1 mM) in 10 ml of water.

PdTu₄I₂. Solid PdI₂ (1 mM) was dissolved in a solution of thiourea (4 mM) in methanol (20 ml) which was then reduced to a small volume and diluted with diethyl ether until precipitation occurred. The product was recrystallized from the hot concentrated aqueous solution by cooling in an ice-bath.

PdTu₄A₂ (A = ClO₄, BF₄, CF₃COO). Freshly prepared Pd(OH)₂ (1 mM) was dissolved at room temperature in a solution of thiourea (4 mM) in 10–15 ml of water containing 2–3 mM of the corresponding acid. The solution was reduced to a small volume and crystalline products were obtained on cooling. A different method has been described⁴ for the preparation of PdTu₄(ClO₄)₂.

PtTuCl₂ · 0.5 H₂O. A solution of K₂PtCl₄ (1 mM) in 13 ml of 4 M HCl was added at room temperature to a solution of thiourea (1 ml) in water (4 ml).

PtTuBr₂ and PtTuI₂. A solution of K₂PtCl₄ (1 mM) in 7 ml of an aqueous solution of HBr or HI at concentrations such as to give a Cl⁻:Br⁻ (or I⁻) ratio of 1:10 was warmed until it was dark brown. When a solution of thiourea (1 mM) in water (4 ml) was added the products precipitated immediately.

$PtTu_2Cl_2$ and $PtTu_4Cl_2$. These were prepared by the method of KURNAKOW³ from K_2PtCl_4 .

$PtTu_2Br_2$ and $PtTu_2I_2$. Solid $PtTuBr_2$ or $PtTuI_2$ (0.5 mM) was suspended in ethanol (12 ml) and solid thiourea (0.5 mM) was added with stirring. The clear solutions obtained were then concentrated until a solid product separated out.

$PtTu_4Br_2$ and $PtTu_4I_2$. The complex $PtTu_4Cl_2$ (0.5 mM) was dissolved in 10 ml of water and 4 ml of 48% HBr or 57% HI were added. The complexes were precipitated by cooling at 0°.

$PtTu_4(ClO_4)_2$ and $PtTu_4(BF_4)_2$. Solid $PtTu_4Cl_2$ (0.6 mM) was dissolved at 50–60° in 4 ml of water and 4 ml of 70% HClO₄ or 31% HBF₄ were added. After cooling, the solid products were washed with very little cold water and ethanol.

$PtTu_4(CF_3COO)_2$. A solution of CF₃COOK (0.8 mM) in 3 ml of ethanol was slowly added to a solution of $PtTu_4(ClO_4)_2$ (0.4 mM) in 4 ml of ethanol. The mixture was cooled with ice overnight and KClO₄ was quantitatively precipitated and filtered off. The solution was concentrated under vacuum and the resulting crystallized complex was washed with ethanol. The perchlorates, fluoborates and trifluoroacetates did not give the complexes MTuA₂ and MTu₃A₂.

Analysis

The following methods were used: (a) palladium — by complexometric titration with a standard 0.01 N aqueous solution of EDTA; (b) platinum — gravimetrically

TABLE I
COLOUR, YIELD AND ANALYTICAL RESULTS FOR COMPLEXES

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

Compound	Colour	Yield (%)	M (%)	S (%)	N (%)
PdTuCl ₂	Orange-yellow	95	41.72 (41.93)	12.46 (12.65)	10.97 (11.04)
PdTu ₂ Cl ₂	Red-brown	72	31.63 (32.28)	19.08 (19.45)	16.72 (16.99)
PdTu ₄ Cl ₂	Orange-red	81	22.04 (22.07)	26.48 (26.60)	23.25 (23.24)
PdTuBr ₂	Red-orange	92	31.10 (31.08)	9.25 (9.37)	8.26 (8.18)
PdTu ₂ Br ₂	Red-brown	69	25.56 (25.42)	15.14 (15.32)	13.19 (13.38)
PdTu ₄ Br ₂	Orange-red	85	18.58 (18.64)	22.35 (22.47)	19.60 (19.64)
Pd ₃ Tu ₇ I ₄ Cl ₂	Red-brown	64	28.23 (28.34)	8.81 (8.54)	7.60 (7.46)
PdTu ₂ I ₂	Red-brown	96	20.64 (20.76)	12.32 (12.51)	10.71 (10.92)
PdTu ₄ I ₂	Orange-red	82	15.93 (16.00)	19.15 (19.29)	16.90 (16.86)
PdTu ₄ (ClO ₄) ₂	Dark yellow	78	17.39 (17.45)	20.84 (21.03)	18.60 (18.37)
PdTu ₄ (BF ₄) ₂	Orange-yellow	65	18.14 (18.19)	21.86 (21.93)	19.12 (19.16)
PdTu ₄ (CF ₃ COO) ₂	Orange	83	16.58 (16.70)	19.89 (20.13)	17.47 (17.59)
PtTuCl ₂ ·0.5 H ₂ O	Lemon yellow	95	55.63 (55.57)	9.16 (9.13)	
PtTu ₂ Cl ₂	Pink-yellow	97	46.52 (46.64)	15.27 (15.33)	
PtTu ₄ Cl ₂	Sulphur yellow	91	34.20 (34.19)	22.40 (22.46)	
PtTuBr ₂	Gold-yellow	95	45.27 (45.26)	7.40 (7.43)	
PtTu ₂ Br ₂	Red-brown	89	38.20 (38.46)	12.44 (12.62)	
PtTu ₄ Br ₂	Yellow	97	29.56 (29.58)	19.29 (19.44)	
PtTuI ₂	Dark brown	94	37.19 (37.15)	6.01 (6.16)	
PtTu ₂ I ₂	Orange-yellow	80	32.38 (32.45)	10.43 (10.66)	
PtTu ₄ I ₂	Orange-yellow	94	25.90 (25.89)	16.94 (17.02)	
PtTu ₄ (ClO ₄) ₂	Lemon yellow	95	27.63 (27.93)	18.23 (18.35)	
PtTu ₄ (BF ₄) ₂	Sulphur yellow	98	29.39 (29.00)	18.92 (19.05)	
PtTu ₄ (CF ₃ COO) ₂	Yellow	97	26.84 (26.88)	17.44 (17.66)	

TABLE II

THIOUREA: METAL RATIOS OBSERVED

Anion (A)	In the solid complexes				By HF titration				By paper chromatography with:					
									Ketones ^e		Alcohols ^f			
	Pd	Pt	Pd ^g	Pt ^g	Ppb	Pd ^c	Pt ^c	Pt ^d	Pd	Pt	Pd	Pt		
Cl ⁻	1	2	4	4	1	2	4	4	1	2	4	4	4	4
Br ⁻	1	2	4	4	1	2	4	4	1	2	4	4	4	4
I ⁻	1 ^g	2	4	4	—	—	—	—	1	2	4	—	—	—
ClO ₄ ⁻	—	—	4	4	1	2	4	—	—	—	—	4	4	4
BF ₄ ⁻	—	—	4	4	1	3	4	—	—	—	—	4	—	—
CF ₃ COO ⁻	—	—	4	4	1	2	4	—	—	—	—	4	4	—

^a In acidic aqueous solution of K₂PdX₄ (X = Cl, Br) or PdA₂ (A = ClO₄, BF₄, CF₃COO).

^b In acidic aqueous solution of K₂PtX₄ (X = Cl, Br, I).

^c In DMF solution of PdTuX₂ (X = Cl, Br).

^d In DMF solution of PtTuX₂ (X = Cl, Br, I).

^e Containing a 1-5 M aqueous solution of NaA (ratios 95:5-80:20).

^f Containing a 4-5 M aqueous solution of HA (ratio 80:20).

^g As 2PdTuI₂·PdTuCl₂.

after combustion of the substance in a quartz vessel; (c) sulphur — gravimetrically as BaSO₄; and (d) nitrogen — by Kjeldhal's method. Analytical results are given in Table I.

Physical measurements

The high frequency (HF) titrations were carried out with a WTW, HFT 3 C type instrument and a HTB 2 cell. In order to avoid hydrolysis, aqueous solutions $1 \cdot 10^{-3} M$ in K₂PdCl₄, Na₂PdBr₄, Pd(ClO₄)₂, Pd(BF₄)₂ and Pd(CF₃COO)₂ and $1 \cdot 10^{-3} M$ in the corresponding acid were titrated with an $8 \cdot 10^{-2} M$ aqueous solution of thiourea. It was not possible to prepare Na₂PdI₄ for these measurements. Aqueous solutions $2 \cdot 10^{-3} M$ in K₂PtCl₄, K₂PtBr₄ and K₂PtI₄ and $2 \cdot 10^{-3} M$ in the corresponding acid were titrated with an $8 \cdot 10^{-2} M$ aqueous solution of thiourea. A $2 \cdot 10^{-3} M$ solution of PdTuCl₂, PdTuBr₂, PtTuCl₂, PtTuBr₂ and PtTuI₂ in dimethylformamide (DMF) was titrated with a $16 \cdot 10^{-2} M$ solution of thiourea in DMF. In all instances, straight lines were obtained, defining very sharply the thiourea:metal ratios indicated in Table II.

The conductivity measurements were carried out with a WTW, LBR-type conductivity bridge and a cell of $K = 0.61$, on $1 \cdot 10^{-3} M$ solutions of the complexes in methanol or DMF and on $1 \cdot 10^{-3} M$ solutions of the complexes in a $0.3 M$ solution of thiourea in the same solvents (Table III).

TABLE III

MOLAR CONDUCTIVITY, $\Lambda_M \Omega^{-1} \cdot \text{cm}^2 \cdot \text{mole}^{-1}$, OF THE COMPLEXES PdTu₄X₂ AND PtTu₄X₂
Concentration = $1 \cdot 10^{-3} M$; temperature = 25°.

Compound	MeOH	MeOH, 0.3 M Tu	DMF	DMF, 0.3 M Tu
PdTu ₄ Cl ₂	129	135	32	45
PdTu ₄ Br ₂	138	149	61	70
PdTu ₄ I ₂	127	166	74	123
PdTu ₄ (ClO ₄) ₂	188	194	145	128
PdTu ₄ (BF ₄) ₂	148	149	148	134
PdTu ₄ (CF ₃ COO) ₂	146	146	70	79
PtTu ₄ Cl ₂	143	142	34	47
PtTu ₄ Br ₂	152	151	70	71
PtTu ₄ I ₂	158	164	111	109
PtTu ₄ (ClO ₄) ₂	189	181	140	124
PtTu ₄ (BF ₄) ₂	Insol.	Insol.	Insol.	Insol.
PtTu ₄ (CF ₃ COO) ₂	152	147	74	80

The chromatography of the complexes was performed with the technique previously described¹. Equivalent amounts of an aqueous solution of ³⁵S-labelled thiourea (0.2 M) and of the complex (0.2 M in thiourea) were mixed together. Samples of 10 μl of these solutions were transferred on a Whatman No. 1 paper strip (8 × 350 mm) and dried at room temperature. The elution was carried out with the single-phase mixtures indicated in Tables IV and V, which give compact spots for both the complex and thiourea.

The quantitative determination of the radioactivity present in the radiochromatograms was performed by scanning the paper strip mounted on a sliding base.

TABLE IV

PAPER CHROMATOGRAPHY OF Pd(II) COMPLEXES WITH THIOUREA (Tu) ADDED WITH FREE ³⁵S-THIOUREA (Tu*) IN ACETONE (Ac), METHYL ETHYL KETONE (MEK), METHANOL, ETHANOL, ISOPROPANOL AND *n*-BUTANOL

Ketones are mixed with an aqueous solution of the sodium salt (NaA), alcohols with an aqueous solution of the acid (HA) in the ratio indicated. Temperature = 25°.

Anion (A)	Solvent (a)	Aq. solution (b)	Ratio a:b	Eluted substance	Tu* complexed	Tu* free	Pd:Tu	R _F complex	R _F Tu
		NaA							
ClO ₄ ⁻	Ac	5 M	95:5	Tu ₃ Pd ²⁺ + 4Tu*	49.1	50.9	1:4	0.92	0.60
ClO ₄ ⁻	Ac	5 M	80:20	Tu ₃ Pd ²⁺ + 4Tu*	50.4	49.6	1:4	0.99	0.80
ClO ₄ ⁻	Ac	1 M	80:20	Tu ₃ Pd ²⁺ + 4Tu*	49.7	50.3	1:4	0.98	0.77
ClO ₄ ⁻	MEK	5 M	95:5	Tu ₃ Pd ²⁺ + 4Tu*	49.5	50.5	1:4	0.77	0.67
ClO ₄ ⁻	MEK	5 M	80:20	Tu ₃ Pd ²⁺ + 4Tu*	50.1	49.9	1:4	0.99	0.87
ClO ₄ ⁻	MEK	1 M	80:20	Tu ₃ Pd ²⁺ + 4Tu*	49.7	50.3	1:4	0.95	0.77
CF ₃ COO ⁻	Ac	5 M	95:5	Tu ₃ Pd ²⁺ + 4Tu*	No separation				
CF ₃ COO ⁻	Ac	5 M	90:10	Tu ₃ Pd ²⁺ + 4Tu*	49.8	50.2	1:4	0.81	0.72
CF ₃ COO ⁻	Ac	5 M	80:20	Tu ₃ Pd ²⁺ + 4Tu*	50.1	49.9	1:4	0.98	0.71
CF ₃ COO ⁻	Ac	1 M	80:20	Tu ₃ Pd ²⁺ + 4Tu*	49.7	50.3	1:4	0.94	0.77
CF ₃ COO ⁻	MEK	5 M	90:10	Tu ₃ Pd ²⁺ + 4Tu*	No separation				
CF ₃ COO ⁻	MEK	5 M	85:15	Tu ₃ Pd ²⁺ + 4Tu*	51.0	49.0	1:4	0.86	0.67
CF ₃ COO ⁻	MEK	5 M	80:20	Tu ₃ Pd ²⁺ + 4Tu*	49.8	50.2	1:4	0.98	0.68
CF ₃ COO ⁻	MEK	1 M	80:20	Tu ₃ Pd ²⁺ + 4Tu*	No separation				
CF ₃ COO ⁻	MEK	2 M	80:20	Tu ₃ Pd ²⁺ + 4Tu*	49.4	50.6	1:4	0.94	0.75
BF ₄ ⁻	Ac	4 M	95:5	Tu ₃ Pd ²⁺ + 4Tu*	49.9	50.1	1:4	0.78	0.45
BF ₄ ⁻	Ac	4 M	80:20	Tu ₃ Pd ²⁺ + 4Tu*	50.6	49.4	1:4	0.97	0.70
BF ₄ ⁻	Ac	1 M	80:20	Tu ₃ Pd ²⁺ + 4Tu*	49.7	50.3	1:4	0.97	0.72
BF ₄ ⁻	MEK	No separation							
		HA							
ClO ₄ ⁻	MeOH	5 M	80:20	Tu ₃ Pd ²⁺ + 4Tu*	50.1	49.9	1:4	0.18	0.57
Cl ⁻	MeOH	4 M	80:20	2TuPd ²⁺ + 2Tu ^a	100.0	—	1:4	0.15	—
Cl ⁻	MeOH	4 M	80:20	Tu ₂ Pd ²⁺ + 2Tu ^b	100.0	—	1:4	0.14	—
Cl ⁻	MeOH	4 M	80:20	Tu ₃ Pd ²⁺ + 4Tu*	49.3	50.8	1:4	0.17	0.60
Cl ⁻	EtOH	4 M	80:20	2TuPd ²⁺ + 2Tu ^a	100.0	—	1:4	0.11	—
Cl ⁻	EtOH	4 M	80:20	Tu ₂ Pd ²⁺ + 2Tu ^b	100.0	—	1:4	0.12	—
Cl ⁻	EtOH	4 M	80:20	Tu ₃ Pd ²⁺ + 4Tu*	49.9	50.1	1:4	0.13	0.62
Cl ⁻	<i>i</i> -PrOH	4 M	80:20	Tu ₃ Pd ²⁺ + 4Tu*	49.8	50.2	1:4	0.07	0.63
Cl ⁻	<i>n</i> -BuOH	4 M	80:20	Tu ₃ Pd ²⁺ + 4Tu*	50.2	49.8	1:4	0.06	0.64
Br ⁻	MeOH	4 M	80:20	2TuPd ²⁺ + 2Tu ^a	100.0	—	1:4	0.12	—
Br ⁻	MeOH	4 M	80:20	Tu ₂ Pd ²⁺ + 2Tu ^b	100.0	—	1:4	0.14	—
Br ⁻	MeOH	4 M	80:20	Tu ₃ Pd ²⁺ + 4Tu*	48.8	51.2	1:4	0.14	0.59

^a 2PdTuX₂ + 2Tu* = PdTu*X₂ + PdX₂, which remains in the starting spot

This was moved at regular intervals past the Geiger-tube window to which a central rectangular slit (10 × 15 mm) was applied. Standard electronic equipment and a Universal lead castle were used. The usual allowance was made for background (about 10 counts/min).

RESULTS AND DISCUSSION

HF titration shows that in aqueous solution palladium(II) and platinum(II) chlorides and bromides and platinum(II) iodide form complexes with thiourea:metal ratios of 1:1, 2:1 and 4:1 as in the solid state. HF titration of the complexes PtTuX₂ (X = Cl, Br, I) in DMF solution with thiourea identified the complexes with ratios of 2:1 and 4:1 while HF titration of PdTuX₂ (X = Cl, Br) in DMF identified the complexes with ratios of 2:1, 3:1 and 4:1 (Table II). Palladium(II) iodide forms only the 2:1 and 4:1 complexes in the solid state. All attempts to prepare the solid 1:1 complex were unsuccessful. No suitable soluble iodide derivative was obtained for HF titration. The very low conductivity of the 1:1 and 2:1 complexes of these halides indicate that they behave as non-electrolytes. Their existence in the solid state and in solution is due to the fact that they can establish halogen bridges in the dimer [TuMX₂]₂ complexes and have two terminal halogen atoms coordinated to the metal in the [Tu₂MX₂] complexes. The solid compound with the composition Pd₃Tu₃I₄Cl₂ corresponds to a stoichiometry of 2PdTuI₂·PdTuCl₂ and may be a polymer. Its molar conductivity ($\Lambda_M = 29.6$) in DMF corresponds to that of a non-electrolyte.

Palladium(II) and platinum(II) perchlorates, fluoborates and trifluoroacetates form only the MTu₄A₂ complexes in the solid state, owing to the low coordinating power of the anions. The HF titration of the aqueous solutions of the Pd(II) perchlorate, fluoborate and trifluoroacetate with thiourea shows the formation of 1:1, 2:1 and 4:1 complexes in solution. The fluoborate gives the 3:1 instead of the 2:1 complex. As palladium(II) salts are easily hydrolyzed, it is likely that in these solutions the 1:1 and 2:1 (or 3:1) thiourea:metal ratios may be due to a fulfilment of the metal coordination by OH⁻ ions rather than by the anions. The platinum(II) perchlorate, fluoborate and trifluoroacetate give in solution the dismutation reaction 2Pt(II) → Pt(0) + Pt(IV) and can therefore not be used for HF titration.

The molar conductivities of the complexes PdTu₄A₂ and PtTu₄A₂ (A = ClO₄, BF₄, CF₃COO) in methanol and PdTu₄(ClO₄)₂, PdTu₄(BF₄)₂ and PtTu₄(ClO₄)₂ in DMF correspond to those of uni-divalent electrolytes⁵. They are practically insensitive to the addition of a large excess of thiourea (25 times that of the complexed thiourea). These complex ions may therefore be considered as being practically undissociated. The molar conductivities of the complexes PdTu₄X₂ (X = Cl, Br, I) in methanol, and still more evidently in DMF, are lower than the value typical of uni-divalent electrolytes in these solvents⁵ and are much more sensitive to the addition of an excess of thiourea. The conductivities of the complexes PtTu₄X₂ (X = Cl, Br, I) are almost normal in methanol, much lower in DMF and practically insensitive to the excess of thiourea.

It is likely, at least for the Pd(II) halide complexes, that the following equilibria occur in solutions:

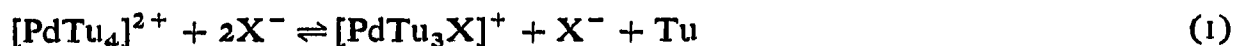


TABLE V

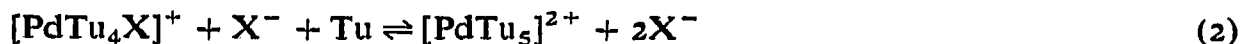
PAPER CHROMATOGRAPHY OF Pt(II) COMPLEXES WITH THIOUREA (Tu) ADDED WITH FREE ³⁵S-THIOUREA (Tu*) IN ACETONE (Ac), METHYL ETHYL KETONE (MEK), METHANOL, ETHANOL, ISOPROPANOL, *n*-BUTANOL AND ISOBUTANOL

Ketones are mixed with an aqueous solution of the sodium salt (NaA), alcohols with an aqueous solution of the acid (HA) in the ratio indicated. Temperature = 21°.

Anion (A)	Solvent (a)	Aq. solution (b)	Ratio a:b	Eluted substance	Tu* complexed free	Pt:Tu	R _F complex	R _F Tu
		NaA						
ClO ₄ ⁻	Ac	5 M	95:5	Tu ₃ Pt ²⁺ + 4Tu*	49.5	1:4	0.85	0.56
ClO ₄ ⁻	Ac	5 M	80:20	Tu ₃ Pt ²⁺ + 4Tu*	49.7	1:4	0.99	0.74
ClO ₄ ⁻	Ac	1 M	80:20	Tu ₃ Pt ²⁺ + 4Tu*	50.1	1:4	0.94	0.68
ClO ₄ ⁻	MEK	5 M	95:5	Tu ₃ Pt ²⁺ + 4Tu*	49.1	1:4	0.77	0.55
ClO ₄ ⁻	MEK	5 M	80:20	Tu ₃ Pt ²⁺ + 4Tu*	50.3	1:4	0.99	0.86
ClO ₄ ⁻	MEK	1 M	80:20	Tu ₃ Pt ²⁺ + 4Tu*	50.4	1:4	0.94	0.80
CF ₃ COO ⁻	Ac	5 M	95:5	Tu ₃ Pt ²⁺ + 4Tu*	No separation			
CF ₃ COO ⁻	Ac	5 M	80:20	Tu ₃ Pt ²⁺ + 4Tu*	50.3	1:4	0.99	0.72
CF ₃ COO ⁻	Ac	1 M	80:20	Tu ₃ Pt ²⁺ + 4Tu*	49.1	1:4	0.90	0.77
CF ₃ COO ⁻	MEK	5 M	95:5	Tu ₃ Pt ²⁺ + 4Tu*	No separation			
CF ₃ COO ⁻	MEK	5 M	80:20	Tu ₃ Pt ²⁺ + 4Tu*	50.7	1:4	0.98	0.67
CF ₃ COO ⁻	MEK	1 M	80:20	Tu ₃ Pt ²⁺ + 4Tu*	No separation			
		HA						
ClO ₄ ⁻	MeOH	5 M	80:20	Tu ₃ Pt ²⁺ + 4Tu*	49.6	1:4	0.18	0.57
Cl ⁻	MeOH	4 M	80:20	2Tu ₃ Pt ²⁺ + 2Tu* ^a	100.0	1:4	0.00	—
Cl ⁻	MeOH	4 M	80:20	Tu ₂ Pt ²⁺ + 2Tu* ^b	100.0	1:4	0.14	—
Cl ⁻	MeOH	4 M	80:20	Tu ₃ Pt ²⁺ + 4Tu*	49.5	1:4	0.15	0.60
Cl ⁻	EtOH	4 M	80:20	Tu ₃ Pt ²⁺ + 4Tu*	50.3	1:4	0.09	0.57
Cl ⁻	EtOH	4 M	80:20	Tu ₃ Pt ²⁺ + 4Tu*	49.8	1:4	0.07	0.58
Cl ⁻	<i>i</i> -PrOH	4 M	80:20	Tu ₃ Pt ²⁺ + 4Tu*	50.1	1:4	0.06	0.61
Cl ⁻	<i>n</i> -BuOH	4 M	80:20	Tu ₃ Pt ²⁺ + 4Tu*	50.3	1:4	0.06	0.67
Cl ⁻	<i>i</i> -BuOH	4 M	80:20	2Tu ₃ Pt ²⁺ + 2Tu* ^a	100.0	1:4	0.12	—
Br ⁻	MeOH	4 M	80:20	Tu ₃ Pt ²⁺ + 2Tu* ^b	100.0	1:4	0.15	—
Br ⁻	MeOH	4 M	80:20	Tu ₃ Pt ²⁺ + 4Tu*	49.8	1:4	0.15	0.59
Br ⁻	EtOH	4 M	80:20	Tu ₃ Pt ²⁺ + 4Tu*	49.3	1:4	0.10	0.61
Br ⁻	<i>i</i> -PrOH	4 M	80:20	Tu ₃ Pt ²⁺ + 4Tu*	50.9	1:4	0.10	0.59
Br ⁻	<i>n</i> -BuOH	4 M	80:20	Tu ₃ Pt ²⁺ + 4Tu*	49.7	1:4	0.12	0.60
Br ⁻	<i>i</i> -BuOH	4 M	80:20	Tu ₃ Pt ²⁺ + 4Tu*	51.1	1:4	0.10	0.61

^a 2PtTuX₂ + 2Tu* = PtTu₂X₂ + PtX₂, which remains in the starting spot.

or



where X = Cl, Br or I.

The strong tendency to coordinate halide ions in a fifth position by $[\text{PdL}_4]^{2+}$ or $[\text{PdNAs}_2]^{2+}$ species (L = N,N'-diphenylthiourea, NAs = 1,8-naphthalene bisdimethylarsine) was demonstrated by conductometric titrations of the corresponding palladium(II) perchlorate complexes with Cl^- ions in non-polar solvents^{4,6} and by their electronic spectra⁴.

The low conductivities of $\text{PdTu}_4(\text{CF}_3\text{COO})_2$ and $\text{PtTu}_4(\text{CF}_3\text{COO})_2$ in DMF are of the same order as the conductivities of the iodide complexes. The trifluoroacetate ion has a coordinating power greater than those of perchlorate and fluoborate ions, as was seen¹ for the thiourea complexes of Zn(II), Cd(II) and Hg(II). The conductivity lowering of the trifluoroacetate complexes in DMF may therefore be attributed, as for the halide complexes, to equilibria of the types in eqns. 1 and 2.

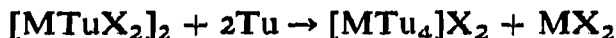
Thiourea complexes of Pd(II) and Pt(II), as with those of Zn(II), Cd(II) and Hg(II)¹ and Cu(I), Ag(I) and Au(I)², very rapidly exchange their coordinated thiourea with free ³⁵S-labelled thiourea in aqueous solution. The kinetics of the exchange could not be studied in this instance either, but the exchange served to identify the composition of the complexes migrating in compact spots on a chromatographic paper strip.

The Pd(II) and Pt(II) complexes, as with those of Cu(I), Ag(I) and Au(I)², can be eluted without decomposition with a mixture of a ketone and an aqueous solution of the sodium salt of the corresponding anion, or with a mixture of an alcohol and an aqueous solution of the corresponding free acid, in the concentrations and ratios indicated in Tables IV and V. The Pd(II) and Pt(II) thiourea complexes are much more stable than those of Zn(II), Cd(II) and Hg(II), which are completely destroyed by the alcohol-acid mixtures¹.

Only the complex ions $[\text{PdTu}_4]^{2+}$ and $[\text{PtTu}_4]^{2+}$ can be eluted without decomposition. Those having lower Tu:M ratios react with free thiourea to give the highest ratio according to the equations:



without any residue of free thiourea on the paper strip, and



forming free metal halide, which remains uneluted in the starting spot on the paper strip.

The elution of the halide complexes in the alcohol mixtures occurs in a medium that contains a great excess of a strong complexing agent such as hydrogen halides (alcohol:4 M HCl or 4 M HBr ratio = 80:20). In these media, the complex ions $[\text{PdTu}_4]^{2+}$ and $[\text{PtTu}_4]^{2+}$ migrate without decomposition and remain separated from the free thiourea for a long time, the R_F values being 0.06-0.17 for the complexes and about 0.6 for thiourea. In such a drastic condition of non-equilibrium between the complex and the free thiourea, no substitution of the coordinated thiourea with the halide ions occurs in the complex. These facts demonstrate that the $[\text{PdTu}_4]^{2+}$ and $[\text{PtTu}_4]^{2+}$ ions are very stable and undissociated in these media, and that of the

two equilibria previously suggested in eqns. 1 and 2 to explain the low conductivity of the halide complexes the equilibrium in eqn. 2 agrees better with the chromatographic data.

In all the ketone mixtures, the R_F values of the complexes are greater than those of thiourea, irrespective of the molarity of the sodium salt:aqueous solution and of the ketone:aqueous solution ratios (Fig. 1). In the alcoholic solutions that contain 4 M or 5 M HA ($A =$ anion of the complex; alcohol:aqueous solution ratio = 80:20),

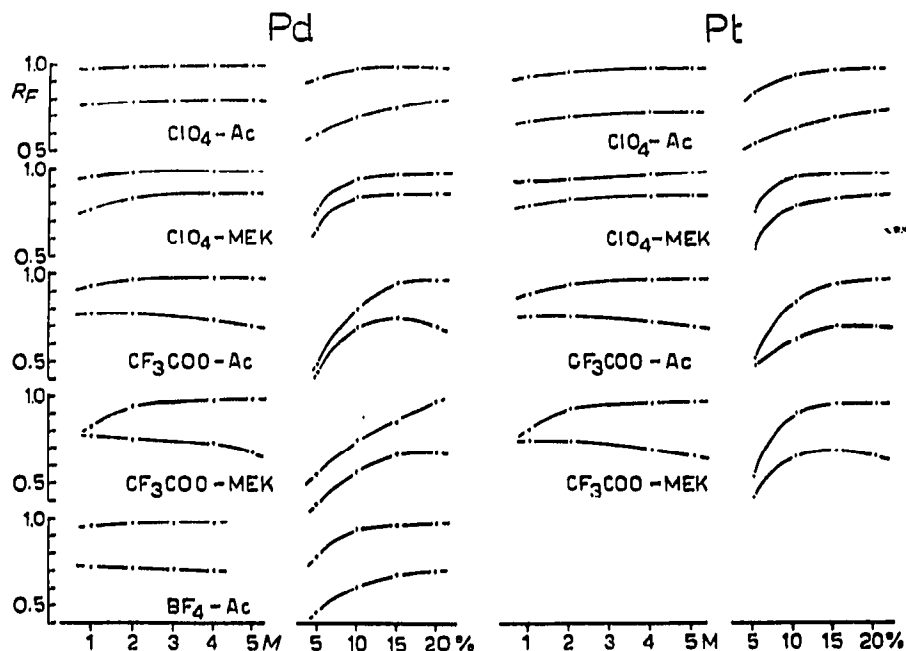


Fig. 1. R_F values observed for the PdTu_4A_2 ($A = \text{ClO}_4, \text{CF}_3\text{COO}, \text{BF}_4$) and PtTu_4A_2 ($A = \text{ClO}_4, \text{CF}_3\text{COO}$) complexes (upper curve) and for thiourea (lower curve) by elution with mixtures of acetone (Ac) or methyl ethyl ketone (MEK) and an aqueous solution of the corresponding sodium salt NaA. For each metal are shown the R_F variations with increasing molarity of the NaA salt in mixtures of ketone and aqueous solution in the ratio 80:20 (left-hand side) and with increasing percentage of the 5 M NaA aqueous solution in the ketone mixture (right-hand side).

thiourea has R_F values comparable with those found in the ketone mixtures with the same solvent:aqueous salt solution ratios. In these alcoholic mixtures, complexes have very low R_F values, mostly lower, in fact, than those of thiourea. As this occurs in systems that contain either free perchloric acid or free hydrogen halides, the lowering of the R_F values of the complexes cannot be ascribed to the complexing action of the halide ions. It may depend on the acidity of the medium or on the availability of the water content of the system, alcohols being more powerful dehydrating agents than ketones. The availability of the water content of the system seems to account for the higher R_F values of the complexes, for, in the ketone mixtures, as the proportion of sodium salt aqueous solution increases, so the R_F values of the complexes increase, while they are almost insensitive to the molarity of the sodium salt in the aqueous solution.

The R_F values of thiourea depend on the ketone and increase as the proportion of aqueous solution in the mixture increases. The R_F values of the trifluoroacetate

complex in the ketone mixtures in some instances decrease as the molarity of the salt solution increases.

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