CHROM. 5736

A PAPER CHROMATOGRAPHIC INVESTIGATION OF THE THIOUREA COMPLEXES OF COPPER(I), SILVER(I) AND GOLD(I)

GIUSEPPE MARCOTRIGIANO, GIORGIO PEYRONEL AND RAFFAELE BATTISTUZZI
Istituto di Chimica Generale e Inorganica, University of Modena, 41 100 Modena (Italy)

(Received September 28th, 1971)

SUMMARY

Several thiourea complexes of formula $M^{I}Tu_{x}A$ (M^{I} = Cu(I), Ag(I) and A = ClO_4, BF_4, CF_3COO, CH_3COO or HCOO; or M^{I} = Au(I) and A = ClO_4, BF_4, CF_3COO, Cl or Br; Tu = thiourea) were prepared; the maximum Tu:M ratio is 3:1 for Cu(I) and Ag(I) and 2:1 for Au(I). The same maximum of 3:1 is observed on high frequency titration of the Ag(I) salts with thiourea in methyl cellosolve. Some of these complexes, undecomposed and in compact spots, may be eluted on chromatographic paper with a mixture of ketones and an aqueous solution of the corresponding sodium salt, or with a mixture of alcohols and an aqueous solution of the corresponding free acid. The Tu:M ratio is 5:2 for Cu(I) perchlorate and fluoroborate in ketones, while it is always 2:1 for the other complexes of Cu(I), Ag(I) and Au(I), irrespective of the anion, the solvent and the amount of aqueous solution in the mixture. The composition of the eluted complexes was determined by a radiochemical method after exchange with ^{35}S-labelled thiourea. The R_F values of the eluted complexes depend on the anion, the solvent and the amount of aqueous solutions in the mixture.

INTRODUCTION

It has previously been shown by LEDERER[1,2] that some metal ions can be eluted by paper chromatography as thiourea complexes by using a mixture of hydrochloric acid and thiourea.

In a previous work[3], we demonstrated that thiourea complexes of zinc(II), cadmium(II) and mercury(II) perchlorates, fluoroborates and trifluoroacetates can be eluted in compact spots on chromatographic paper by using a mixture of a ketone and a 5 *M* aqueous solution of the sodium salt of the corresponding anion. The number of thiourea molecules per metal atom in the migrating complex increases from zinc to mercury approximately in accordance with the increase in their affinities for sulphur.

We have now extended this method to the study of the thiourea complexes of copper(I), silver(I) and gold(I), in order to compare their chromatographic behaviour with that of the group IIB metals, with reference to their class B character and their coordination ability.

EXPERIMENTAL

Reagents of the best commercial grade were used for the preparation of the solid complexes and in all the measurements.

Preparation of the complexes

The copper(I) and silver(I) complexes were prepared by dissolving copper(I) oxide and silver oxide in a slight excess of a 4 *M* aqueous solution of the corresponding acid containing thiourea (Tu) in the same stoichiometric ratio as in the solid complex to be prepared. The crystalline complex was obtained by concentrating the solution under vacuum. The silver acetate complexes were prepared by dissolving silver acetate in 50 % acetic acid containing three equivalents of thiourea; large crystals of $AgTu_3(CH_3COO)\cdot 2CH_3COOH$ were obtained by cooling this solution with ice. These crystals, when kept for about twelve days under vacuum over potassium hydroxide, lose the two CH_3COOH molecules and the complex $AgTu_3(CH_3COO)$ is obtained.

The bis(thiourea)gold(I) fluoroborate, trifluoroacetate, bromide and iodide complexes were obtained by dissolving at room temperature 1 mmole of freshly prepared gold(III) hydroxide in 5 ml of an aqueous solution containing the stoichiometric amount of the corresponding acid and 4 mmoles of thiourea. In all cases free sulphur was separated as an oxidation product of thiourea by gold(III) which was reduced to gold(I). After filtration of the solid products and overnight cooling of the solution with ice, colourless crystals of the complexes were obtained.

Bis(thiourea)gold(I) chloride was prepared by addition of 4 mmole of thiourea to the aqueous solution of 1 mmole of $HAuCl_4\cdot 4H_2O$. Colourless crystals were obtained by cooling the solution with ice. Bis(thiourea)gold(I) perchlorate was obtained as colourless needles by cooling with ice a concentrated solution of bis (thiourea)gold(I) chloride in a 40 % aqueous solution of perchloric acid.

The complexes were analysed by conventional methods (copper by EDTA; silver by Volhard titration; gold gravimetrically as the metal after combustion; sulphur as barium sulphate; nitrogen by the Kjeldahl method; water by weight loss over phosphorus pentoxide; free acetic acid by weight loss over potassium hydroxide). The results are given in Table I.

High frequency measurements

High frequency measurements were carried out only on the silver(I) complexes which in the solid state show the greatest variety of Tu:Ag ratios. Using a WTW apparatus (Wissenschaftliche Technische Werkstätten, Weilheim/Obb., G.F.R.) at a frequency of 30 MHz ±1 % and a 10-ml semimicro cell made of titanate ceramics, a 2 m*M* solution of AgTuA ($A=ClO_4,BF_4,CF_3COO$) in methyl cellosolve was titrated with a 80 m*M* solution of thiourea in the same solvent by the deflection method. The Tu:Ag ratios determined in the solutions by this method are given in Table II.

Paper chromatography with ^{35}S-thiourea

Equal volumes of aqueous solutions of ^{35}S-labelled thiourea (Tu*) and of the complex used, isotonic in the free and complexed thiourea, were mixed. A 10 μl volume of the resulting solution was dried at room temperature on a Whatman No. 1 paper strip (0.8 × 35 cm) and the spot eluted with single-phase solvent mixtures of a

TABLE I

ANALYTICAL DATA FOR THE COMPLEXES

Compound	*Found* (%)			*Calculated* (%)		
	Metal	*N*	*S*	*Metal*	*N*	*S*
$CuTu_2ClO_4\cdot H_2O$[a]	19.10	16.72	19.36	19.06	16.80	19.24
$Cu_2Tu_5(ClO_4)_2\cdot H_2O$[b]	17.68	19.29	21.58	17.53	19.32	22.08
$CuTu_3ClO_4$	16.04	21.56	24.31	16.23	21.46	24.57
$CuTu_2BF_4\cdot H_2O$[c]	19.64	17.23	19.71	19.81	17.16	20.00
$CuTu_3BF_4$	16.56	22.26	25.37	16.78	22.16	25.39
$CuTu_3CF_3COO$	15.50	21.03	23.50	15.69	20.75	23.75
$CuTu_3HCOO\cdot 2H_2O$	17.13	22.53	25.31	17.03	22.52	25.74
$CuTu_3CH_3COO$	18.06	23.95	27.31	18.10	23.94	27.40
$AgTuClO_4$	38.12	9.85	11.12	38.05	9.84	11.31
$Ag_2Tu_3(ClO_4)_2$	33.48	13.08	14.67	33.55	13.06	14.95
$AgTu_3ClO_4$	24.46	19.35	21.16	24.75	19.28	21.08
$AgTuBF_4$	39.80	10.26	11.62	39.83	10.34	11.84
$Ag_2Tu_3(BF_4)_2$	34.83	13.39	15.28	34.92	13.59	15.57
$AgTu_3BF_4$	25.47	19.99	22.57	25.49	19.86	22.78
$AgTuCF_3COO$	36.25	9.51	10.52	36.32	9.43	10.79
$Ag_2Tu_3(CF_3COO)_2$	32.06	12.68	14.10	32.19	12.53	14.35
$AgTu_3CF_3COO$	23.98	18.81	21.24	24.01	18.70	21.41
$AgTu_3HCOO\cdot 2H_2O$[d]	25.79	20.20	22.51	25.85	20.13	23.05
$AgTu_3CH_3COO$	27.38	21.16	24.12	27.29	21.25	24.33
$AgTu_3CH_3COO\cdot 2CH_3COOH$[e]	21.03	16.46	19.20	20.93	16.31	18.67
$AuTu_2ClO_4\cdot H_2O$	42.02	11.58	13.62	42.21	12.00	13.74
$AuTu_2BF_4\cdot H_2O$	43.29	12.16	13.92	43.38	12.33	14.12
$AuTu_2CF_3COO\cdot H_2O$	40.72	11.50	13.11	41.01	11.66	13.35
$AuTu_2Cl$	51.12	14.42		51.20	14.55	
$AuTu_2Br$	45.92	12.96		45.90	13.05	
$AuTu_2I$	41.36	11.68		41.36	11.76	

[a] H_2O: found 5.23, calculated 5.40%.
[b] H_2O: found 2.36, calculated 2.48%.
[c] H_2O: found 5.50, calculated 5.61%.
[d] H_2O: found 7.21, calculated 8.61%.
[e] Acetic acid: found 22.94, calculated, 23.29%.

TABLE II

THIOUREA : METAL RATIOS OBSERVED

Anion (*A*)	*In the solid complexes*			*By H.F. titration in methyl cellosolve*	*By paper chromatography with*					
					Ketones[a]			*Alcohols*[b]		*Water*[c]
	Cu+	*Ag*+	*Au*+	*Ag*+	*Cu*+	*Ag*+	*Au*+	*Cu*+	*Ag*+	*Au*+
ClO_4^-	2;2.5;3	1;1.5;3	2 (H_2O)	1.5;2;3	2.5	2	2	2	2	
BF_4^-	2 3	1;1.5;3	2 (H_2O)	1.5;2;3	2.5	2	2	2		
CF_3COO^-	3	1;1.5;3	2 (H_2O)	1.5;2;3	2	2	2	2		
CH_3COO^-	3	3						2	2	
$HCOO^-$	3	3						2	2	
Cl^-			2							2
Br^-			2							2
I^-			2							

[a] Containing a 5 *M* aqueous solution of NaA (ratios: 95:5–80:20).
[b] Containing a 5 *M* aqueous solution of HA (ratio: 80:20).
[c] Aqueous solution of sodium halide (0.5 and 1.0 *M*).

ketone and a 5 *M* aqueous solution of the sodium salt of the anion contained in the complex, or mixtures of an alcohol and a 5 *M* aqueous solution of the corresponding acid. For the $AuTu_2X$ ($X = Cl, Br$) complexes, 0.5 and 1.0 *M* aqueous solutions of sodium chloride or bromide were used. For $AuTu_2Cl$, a good chromatographic separation of the complex from thiourea can also be obtained with an 80:20 mixture of alcohol and 4 *M* hydrochloric acid.

Preliminary experiments showed that in all the solvent mixtures used, the exchange of complexed and free thiourea is instantaneous and complete, irrespective of the anion contained in the mixture. The possibility of the anion having an inductive effect on the thiourea exchange can therefore be excluded. It has been shown[4] that the ligand exchange between free labelled ethylenediamine and complexed ethylenediamine in $(Auen_2)^{3+}$ in aqueous solution is accelerated by the addition of chloride ion but not of perchlorate ion because of the greater coordination effect of the former. In the case of gold(I)thiourea complexes, the thiourea exchange is just as rapid with low-complexing anions such as ClO_4^- as it is with high-complexing anions such as halides.

Owing to this immediate thiourea exchange, the composition of the stable complexes migrating in compact spots on the paper strip was determined by the equation $MTu_x + xTu^* = MTu^*_y + (2x - y)Tu^*$. The radioactivities of the migrating spots were measured by moving the paper strips, mounted on a sliding base, 1 cm at a time under the end window of a Geiger–Müller counter, to which a central rectangular slit 1 cm wide was applied. The results are given in Tables III, IV and V.

RESULTS AND DISCUSSION

The thiourea:metal ratios observed for the copper(I) and silver(I) complexes, whether in the solids or determined by H.F. titration for silver (I), are more variable and reach a greater value(3:1) than for the gold(I) complexes (2:1).

Paper chromatography shows that definite thiourea complexes of the univalent ions of the IB subgroup can migrate in compact spots on the paper strip. The metal: thiourea ratio of the migrating complex is always independent of the M:Tu ratio of the starting mixture.

The thiourea complex of copper(I) perchlorate and fluoroborate, eluted with mixtures of a ketone and a 5 *M* aqueous solution of the sodium salt (ratio 80:20), has a thiourea: metal ratio (5:2) greater than that of the copper(I) trifluoroacetato complex (2:1) eluted with the same single-phase solvent mixtures. This different behaviour may be ascribed to the greater complexing action of the trifluoroacetate ion, as has already been observed for the corresponding complexes of the IIB subgroup[3].

On the other hand, by using a mixture of an alcohol and a 5 *M* aqueous solution of the corresponding acid in the ratio 80:20 for the elution of the copper(I) complexes, the thiourea: metal ratio is always 2:1, irrespective of the anion. This shows that alcohols have a greater competitive action than ketones. This competitive action may act in solvating the thiourea molecules rather than in coordinating the metal ion.

On elution, silver(I) and gold(I) thiourea complexes always give the same thiourea:metal ratio (2:1), irrespective of the anion, the solvent (ketone or alcohol), the solvent:aqueous solution ratio and the reagent present in aqueous solution (sodium salt in the case of ketones and free acid in the case of alcohols).

TABLE III

PAPER CHROMATOGRAPHY OF COPPER (I) COMPLEXES WITH THIOUREA (Tu) ADDED WITH FREE ^{35}S-THIOUREA (Tu*) IN ACETONE (Ac), METHYL ETHYL KETONE (MEK), METHANOL, ETHANOL, ISOPROPANOL, ISOBUTANOL AND ISOAMYL ALCOHOL

Ketones are mixed with a 5 *M* aqueous solution of the sodium salt (ratio 80:20); alcohols with a 5 *M* aqueous solution of the acid (ratio 80:20).

Anion	*Solvent*	*Eluted substance*	Tu^*, *complex*	Tu^*, *free*	*Cu*:*Tu*	R_F, *complex*	R_F, *Tu*
ClO_4^-	Ac	$Tu_2Cu^+ + 2Tu^*$	62.7	37.3	2:5	0.97	0.72
ClO_4^-	Ac	$Tu_3Cu^+ + 3Tu^*$	41.9	58.1	2:5	0.97	0.72
ClO_4^-	Ac	$Tu_5^*Cu_2^{++}$	100.0		2:5	0.97	
ClO_4^-	MEK	$Tu_2Cu^+ + 2Tu^*$	65.2	34.8	2:5	0.98	0.84
ClO_4^-	MEK	$Tu_3Cu^+ + 3Tu^*$	41.9	58.1	2:5	0.98	0.84
ClO_4^-	MEK	$Tu_5^*Cu_2^{++}$	100.0		2:5	0.98	
ClO_4^-	MeOH	$Tu_2Cu^+ + 2Tu^*$	50.4	49.3	1:2	0.10	0.52
ClO_4^-	MeOH	$Tu_3Cu^+ + 3Tu^*$	33.9	66.1	1:2	0.10	0.52
ClO_4^-	MeOH	$Tu_5^*Cu_2^{++}$	80.8	19.1	1:2	0.10	0.52
ClO_4^-	EtOH	$Tu_2Cu^+ + 2Tu^*$	53.1	46.9	1:2	0.06	0.50
ClO_4^-	EtOH	$Tu_3Cu^+ + 3Tu^*$	35.3	64.7	1:2	0.06	0.50
ClO_4^-	EtOH	$Tu_5^*Cu_2^{++}$	81.2	18.8	1:2	0.06	0.50
ClO_4^-	*i*-PrOH	$Tu_2Cu^+ + 2Tu^*$	51.1	48.9	1:2	0.06	0.45
ClO_4^-	*i*-PrOH	$Tu_3Cu^+ + 3Tu^*$	34.8	65.2	1:2	0.06	0.45
ClO_4^-	*i*-PrOH	$Tu_5^*Cu_2^{++}$	80.5	19.5	1:2	0.06	0.45
ClO_4^-	*i*-BuOH	$Tu_2Cu^+ + 2Tu^*$	50.2	49.8	1:2	0.05	0.52
ClO_4^-	*i*-BuOH	$Tu_3Cu^+ + 3Tu^*$	34.8	65.2	1:2	0.05	0.52
ClO_4^-	*i*-BuOH	$Tu_5^*Cu_2^{++}$	80.8	19.2	1:2	0.05	0.52
ClO_4^-	*i*-AmOH	$Tu_2Cu^+ + 2Tu^*$	49.6	50.4	1:2	0.04	0.47
ClO_4^-	*i*-AmOH	$Tu_3Cu^+ + 3Tu^*$	32.8	67.2	1:2	0.04	0.47
ClO_4^-	*i*-AmOH	$Tu_5^*Cu_2^{++}$	81.3	18.7	1:2	0.04	0.47
BF_4^-	Ac	$Tu_2Cu^+ + 2Tu^*$	61.3	38.8	2:5	0.98	0.72
BF_4^-	Ac	$Tu_3Cu^+ + 3Tu^*$	40.2	59.8	2:5	0.98	0.72
BF_4^-	MeOH	$Tu_3Cu^+ + 3Tu^*$			1:2	0.15	0.44
BF_4^-	EtOH	$Tu_3Cu^+ + 3Tu^*$			1:2	0.09	0.44
BF_4^-	*i*-PrOH	$Tu_3Cu^+ + 3Tu^*$			1:2	0.07	0.43
BF_4^-	*i*-BuOH	$Tu_3Cu^+ + 3Tu^*$			1:2	0.03	0.50
BF_4^-	*i*-AmOH	$Tu_2Cu^+ + 2Tu^*$	51.3	48.7	1:2	0.00	0.41
BF_4^-	*i*-AmOH	$Tu_3Cu^+ + 3Tu^*$	34.2	65.8	1:2	0.00	0.41
CF_3COO^-	Ac	$Tu_3Cu^+ + 3Tu^*$	33.8	66.2	1:2	0.97	0.74
CF_3COO^-	MEK	$Tu_3Cu^+ + 3Tu^*$	34.8	65.2	1:2	0.97	0.69
CF_3COO^-	*i*-AmOH	$Tu_3Cu^+ + 3Tu^*$	34.6	65.4	1:2	0.09	0.21
CH_3COO^-	*i*-AmOH	$Tu_3Cu^+ + 3Tu^*$	33.0	67.0	1:2	0.00	0.27
$HCOO^-$	*i*-AmOH	$Tu_3Cu^+ + 3Tu^*$	33.9	66.1	1:2	0.00	0.24

Bearing in mind that the complex and free thiourea migrate separately on the paper strip and therefore are not in equilibrium, the constancy of the ratio Tu:M = 2:1 observed for the three metal ions indicates that the coordination number 2 (presumably linear by *s–p* hybridization) is more stable for these thiourea complexes. This stability is much greater than that of the corresponding complexes of the divalent ions of the IIB subgroup, as these are completely decomposed by elution with the same alcohol mixtures[3].

In the mixtures of ketones and 5 *M* aqueous solution of the sodium salt, the R_F values of the thiourea complexes of copper(I), silver(I) and gold(I) are always higher than those of thiourea, as for the corresponding zinc(II), cadmium(II) and mercury(II) complexes[3]. In mixtures of alcohols and 5 *M* aqueous solutions of the free acid, the

TABLE IV

PAPER CHROMATOGRAPHY OF Tu_xAg^+ ADDED WITH FREE ^{35}S-THIOUREA (Tu^*) IN ACETONE (Ac) MIXED WITH A 5 *M* AQUEOUS SOLUTION OF THE SODIUM SALT (RATIO 80:20) OR IN ALCOHOL MIXED WITH A 5 *M* AQUEOUS SOLUTION OF THE FREE ACID (RATIO 80:20)

Anion	*Solvent*[a]	*Eluted substance*	*Tu*, complex*	*Tu*, free*	*Ag:Tu*	*R_F, complex*	*R_F, Tu*
ClO_4^-	Ac	$TuAg^+ + Tu^*$	100.0		1:2	0.93	
ClO_4^-	Ac	$Tu_3Ag^+ + 3Tu^*$	33.2	66.8	1:2	0.93	0.72
ClO_4^-	MeOH	$TuAg^+ + Tu^*$	100.0		1:2	0.09	
ClO_4^-	MeOH	$Tu_3Ag^+ + 3Tu^*$	33.3	66.7	1:2	0.09	0.52
ClO_4^-	EtOH	$TuAg^+ + Tu^*$	100.0		1:2	0.09	
ClO_4^-	EtOH	$Tu_3Ag^+ + 3Tu^*$			1:2	0.05	0.49
ClO_4^-	*i*-PrOH	$TuAg^+ + Tu^*$	100.0		1:2	0.07	
ClO_4^-	*i*-PrOH	$Tu_3Ag^+ + 3Tu^*$			1:2	0.07	0.49
ClO_4^-	*i*-BuOH	$TuAg^+ + Tu^*$	100.0		1:2	0.06	
ClO_4^-	*i*-BuOH	$Tu_3Ag^+ + 3Tu^*$			1:2	0.00	0.50
ClO_4^-	*i*-AmOH	$TuAg^+ + Tu^*$	100.0		1:2	0.07	
ClO_4^-	*i*-AmOH	$Tu_3Ag^+ + 3Tu^*$	33.8	66.2	1:2	0.08	0.47
BF_4^-	Ac	$TuAg^+ + Tu^*$	100.0		1:2	0.97	
BF_4^-	Ac	$Tu_3Ag^+ + 3Tu^*$	34.0	66.0	1:2	0.97	0.71
CF_3COO^-	Ac	$TuAg^+ + Tu^*$	Insoluble				
CF_3COO^-	Ac	$Tu_3Ag^+ + 3Tu^*$	32.5	67.5	1:2	0.97	0.74
CH_3COO^-	*i*-AmOH	$Tu_3Ag^+ + 3Tu^*$	34.7	65.3	1:2	0.00	0.22
$HCOO^-$	*i*-AmOH	$Tu_3Ag^+ + 3Tu^*$	33.0	67.0	1:2	0.00	0.21

[a] Abbreviations as in Table III.

TABLE V

R_F VALUES FOR THE COMPLEXES Tu_2AuA AND THIOUREA (Tu) ELUTED WITH MIXTURES OF A KETONE AND A 5 *M* AQUEOUS SOLUTION OF THE NaA SALT IN THE INDICATED MIXTURE RATIO

For halides, a 0.5 *M* or 1.0 *M* aqueous solution of sodium halide was used. Starting mixture of eluted substances: $Tu_2AuA + 2Tu^*$. Measured radioactivities of the eluted species: $Tu_2^*Au^+$ (49.3–50.9%); free Tu^* (49.1–50.9%).

Anion (A)	*Mixture ratio*	*Acetone*		*Methyl ethyl ketone*		*Acetylacetone*		*Water*	
		Complex	*Tu*	*Complex*	*Tu*	*Complex*	*Tu*	*Complex*	*Tu*
ClO_4^-	95:5	0.93	0.67	0.92	0.79				
ClO_4^-	90:10	0.97	0.69	0.95	0.80	0.54	0.41		
ClO_4^-	85:15	0.98	0.71	0.96	0.81	0.65	0.44		
ClO_4^-	80:20	0.99	0.73	0.97	0.83	0.83	0.49		
BF_4^-	95:5	0.74	0.50	0.68	0.33				
BF_4^-	90:10	0.92	0.61	0.75	0.51				
BF_4^-	85:15	0.96	0.66	0.79	0.57				
BF_4^-	80:20	0.98	0.67	0.84	0.60				
CF_3COO^-	95:5	0.78	0.67	0.55	0.35				
CF_3COO^-	90:10	0.87	0.72	0.75	0.54				
CF_3COO^-	85:15	0.92	0.75	0.87	0.63	0.50	0.37		
CF_3COO^-	80:20	0.96	0.74	0.95	0.69	0.60	0.36		
Cl^-	0.5 *M* NaCl							0.31	0.68
Cl^-	1.0 *M* NaCl							0.29	0.69
Br^-	0.5 *M* NaBr							0.30	0.69
Br^-	1.0 *M* NaBr							0.27	0.70

R_F values of the copper(I) and silver(I) complexes are always very much lower than those of thiourea. This behaviour could depend on the fact that a certain amount of water is essential in the mixture to give high R_F values for the complexes, as is shown by their variation with the solvent: aqueous solution ratios. Alcohols, which are better dehydrating solvents than ketones, apparently reduce the availability of the water present in the system and consequently reduce the migrating velocity of the complexes.

The R_F variations of the gold(I) complexes, explored for ketone: aqueous solution ratios varying from 95:5 to 80:20 (Table V), depend on the anion, the ketone and the aqueous solution present in the single-phase solvent mixture used as eluent. Their values decrease in the approximate order $ClO_4^- > BF_4^- > CF_3COO^-$ and acetone > methyl ethyl ketone > acetylacetone, and increase with increasing amounts of aqueous solution in the system.

ACKNOWLEDGEMENT

This work was supported by financial aid from the Consiglio Nazionale delle Ricerche of Italy.

REFERENCES

1 M. Lederer, *J. Chromatogr.*, 4 (1960) 414.
2 M. Lederer, *J. Chromatogr.*, 7 (1962) 366.
3 G. Peyronel, G. Marcotrigiano and R. Battistuzzi, in press.
4 D. S. Popplewell and R. G. Wilkins, *J. Chem. Soc.*, (1955) 4098.