REACTIONS OF CHLOROPLATINUM(IV) COMPLEX WITH THIOUREA AND ITS ALKYL DERIVATIVES

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Reaction of the $PtCl_6^{2-}$ ions with thiourea, N-methyl-, N,N'-dimethyl-, and N,N,N'-trimethylthiourea, respectively, led to complexes analogous to those formed on the reaction of the $PtCl_4^{2-}$ ion with these ligands. Formamidine disulfide or its alkyl derivatives were identified as the oxidation products. N,N,N',N'-Tetramethylthiourea and N,N'-ethylenethiourea afforded in the same conditions the Pt(IV) complexes; reduction of Pt(IV) to Pt(II) was not observed.

Thiourea and its derivatives hold a prominent position among organic sulfur-containing ligands in coordination chemistry. Of interest are their complexing properties, and their effects particularly in substitution and oxidation-reduction reactions of their complexes. Complexes of thiourea with platinum have been extensively investigated[1-5]; attention has been paid particularly to substitution reactions of platinum(II) complexes, in which thiourea exerts a strong *trans* effect[6,7], reactions of platinum(IV) complexes with thiourea and its derivatives have been studied to a lesser extent too[1,8-10].

It has been shown[11-14] that thiourea as a ligand in chlorocupric complex affects the Cu—Cl bond in such a manner that the bond is homolytically cleaved. The strong *trans* effect of thiourea in platinum(II) compounds and its pronounced effect on the intracomplex redox conversions in cupric complexes, associated with the mutual influence of the ligands, stimulated further interest in the reactions of thiourea and its derivatives with platinum(IV) complexes.

EXPERIMENTAL

Chemicals: Thiourea *p.a.* (Lachema, Brno), alkylthioureas *p.a.* (Fluka), potassium chloroplatinate(IV) and chloroplatinate(II) *p.a.* Formamidine disulfide and its alkyl derivatives were prepared by oxidation of thiourea and its respective alkyl derivatives with $SOCl_2$ in chloroform[15].

Platinum complexes with the following ligands were prepared: thiourea (tu), N-methylthiourea (CH_3tu), N,N'-dimethylthiourea [$(CH_3)_2tu$], N,N,N'-trimethylthiourea [$(CH_3)_3tu$] (labelled L in the formulas); N,N,N',N'-tetramethylthiourea [$(CH_3)_4tu$], N,N'-ethylenethiourea [$(CH_2)_2tu$] (labelled L' in the formulas).

The complexes were prepared by reaction of aqueous solutions of K_2PtCl_6 acidified with hydrochloric acid with solutions of the ligands in methanol. The platinum-to-ligand molar ratios 1 : 4 and 1 : 6 were applied using the same experimental conditions, particularly the temperature, which was controlled so that it not exceed 60°C. The preparation of the complexes from aqueous solutions of K_2PtCl_4 was carried out according to[2,3], and the products served as reference substances. Most of the complexes prepared occurred in microcrystalline form.

Complexes of the types $Pt_2L_4Cl_6$ (*II*, *IV*, *VI*, *IX*) and PtL'_2Cl_4 (*X*, *XI*) (Table I) were precipitated from the solutions and after 20 min they were isolated, washed with cold distilled water, methanol, and ether, and dried in a dessicator above KOH. The substances are low soluble in water and in organic solvents. The yields were 90—95%. The pairs of substances prepared using the two platinum-to-ligand ratios were analyzed and found to be identical.

Complexes of the types PtL_4Cl_2 (*I*, *III*, *V*, *VII*) and PtL_2Cl_2 (*VIII*) (Table I) were prepared either by dissolving the $Pt_2L_4Cl_6$ complexes in methanolic solutions of the corresponding ligands or by reaction of aqueous solution of potassium chloroplatinate(IV) with methanolic solutions of the ligands using the platinum-to-ligand molar ratios 1 : 6 and 1 : 8; after the end of the reaction, indicated by dissolution of the intermediate product $Pt_2L_4Cl_6$, the solvent was partly evaporated at 40°C and the substance was precipitated with cyclohexane, washed with ether, and dried above KOH. The freshly prepared complexes are soluble in water, alcohol, and acetone, and insoluble in ether and cyclohexane.

The attempted preparation of the substance *VII* led to a mixture, probably of the substances *VII* and *VIII*, rather than to a single chemical, which is in accordance with the data of[2]. When the mixture in the original solution was heated to 60°C or was allowed to stand for 24 h at room temperature, the pure substance *VIII* resulted.

All complexes listed in Table I were prepared from potassium chloroplatinate(IV); the complexes obtained from the reaction of potassium chloroplatinate(II) with the ligands served as reference substances. Their analyses and spectral data (UV, IR) indicate their identity with the

TABLE I

Analyses of the Complexes Prepared

Complex	Designation	Colour	% Pt		% S		% Cl	
			calc.	found	calc.	found	calc.	found
$Pt(tu)_4Cl_2$	*I*	yellow	34·20	33·82	22·48	22·03	12·43	13·07
$Pt_2(tu)_4Cl_6$	*II*	redbrown	43·00	42·92	14·13	13·84	23·44	23·21
$Pt(CH_3tu)_4Cl_2$	*III*	yellow	31·14	31·22	20·47	20·04	11·32	11·52
$Pt_2(CH_3tu)_4Cl_6$	*IV*	orange-red	40·50	39·76	13·31	13·79	22·08	22·85
$Pt[(CH_3)_2tu]_4Cl_2$	*V*	yellow-brown	28·58	28·18	18·79	17·98	10·39	11·12
$Pt_2[(CH_3)_2tu]_4Cl_6$	*VI*	orange-red	38·27	38·18	12·58	12·86	20·86	21·90
$Pt[(CH_3)_3tu]_4Cl_2$	*VII*	yellow-brown	26·41	32·45	17·36	—	9·60	—
$Pt[(CH_3)_3tu]_2Cl_2$	*VIII*	yellow-brown	38·83	38·67	12·76	12·70	14·11	14·92
$Pt_2[(CH_3)_3tu]_4Cl_6$	*IX*	orange-red	36·27	36·89	11·92	12·33	19·77	20·80
$Pt[(CH_3)_4tu]_2Cl_4$	*X*	orange-red	32·41	32·14	10·65	10·71	23·56	23·27
$Pt[(CH_2)_2tu]_2Cl_4$	*XI*	yellow-brown	36·05	35·08	11·85	12·14	26·20	26·35

complexes *I*, *III*, *V*, and *VIII*. The complexes PtL'_2Cl_2 (*XII*, *XIII*), prepared and analyzed in[10], were, however, different from the substances *X* and *XI*, respectively.

After filtering the complexes off, the oxidation products of the ligands were identified in the filtrates by thin layer chromatography on Silufol plates; the spots were developed with iodine vapours and ammonia. The R_F values of the products examined and of the standards are given in Table II.

RESULTS AND DISCUSSION

The reactions studied can be written as:

$$2\,K_2PtCl_6 + 6\,L = Pt_2L_4Cl_6 + 4\,KCl + [L—L].2\,HCl \qquad (A)$$

$$Pt_2L_2Cl_6 + 6\,L = 2\,PtL_4Cl_2 + [L—L].2\,HCl \qquad (B)$$

$$K_2PtCl_6 + 2\,L' = PtL'_2Cl_4 + 2\,KCl \qquad (C)$$

$$K_2PtCl_4 + 4\,L = PtL_4Cl_2 + 2\,KCl \qquad (D)$$

$$K_2PtCl_4 + 2\,L\,(L') = PtL_2Cl_2\,(PtL'_2Cl_2) + 2\,KCl\,. \qquad (E)$$

([L—L] is formamide disulfide or formamidine derivative disulfide, in the text referred to as compound *XIV*).

TABLE II

R_F Values of the Standards and of the Substances Examined
Eluent: acetone–water–acetic acid 1 : 2 : 1 (vol.).

Substance	Thiourea		Disulfide	
	standard	found	standard	found
tu	0·73	0·75	0·55	0·57
CH_3tu	0·72	0·70	0·51	0·54
$(CH_3)_2tu$	0·71	0·71	0·39	0·40
$(CH_3)_3tu$	0·71	0·74	0·32	0·33
$(CH_3)_4tu$[a]	0·80	0·84	—	—
$(CH_2)_2tu$[a]	0·81	0·82	—	—

[a] Eluent: acetone–water 1 : 3 (vol.).

The reaction (A) is an oxidation–reduction process, leading originally to the platinum(II)–platinum(IV) complex $Pt_2L_4Cl_6$ or $[PtL_4][PtCl_6]$. Increase in the concentration of the ligand L is in favour of the complete reduction of Pt(IV) to Pt(II) (reaction (B)). The reactions (A) and (B) gave rise to the complexes *I* to *IX*. The reaction (C) is a substitution reaction, not involving oxidation-reduction conversion; the complexes *X* and *XI* were prepared according to it. The reactions (D) and (E) were employed to obtain the reference platinum(II) complexes. In the case of the reduction of Pt(IV) to Pt(II) during the formation of the complexes *I*–*IX* on the action of the respective ligands, the substance *XIV* was detected in the solutions by means of TLC; in contrast to this, the substance *XIV* was not found during the preparation of the complexes *X* and *XI*, only the starting ligands were present. In these systems, no other substances that might represent decomposition products of the corresponding disulfides were identified either; this remained true even when the solvent polarity was altered.

Knowing the oxidation-reduction potentials of the systems formamidine disulfide/thiourea[16], Pt(IV)/Pt(II), and $Pt(II)/Pt^0$ (refs[17–19]), we could expect oxidation-reduction processes to occur during the reactions of the Pt(IV), Pt(II) chloro complexes with thiourea. However, it follows from works dealing with reactions of thiourea with Pt(II) complexes[7] that thiourea does not induce any oxidation–reduction changes in platinum(II) complexes. The authors of the paper[20] suggest that introduction of a ligand possessing electron donor properties results in a lowering of the redox potential of the system $Pt(IV)/Pt(II)/Pt^0$. In the system under study, the entering of thiourea into the coordination sphere of the Pt(II) complex probably affects the potential of the system to such an extent that Pt(II) is unable to oxidize thiourea to formamidine disulfide.

On the other hand, the entering of thiourea into the coordination sphere of chloroplatinum(IV) complex induces an oxidation–reduction conversion.

Attempts to prove liberation of elemental chlorine during the reaction of K_2PtCl_6 with thiourea, as a consequence of the mutual influence of thiourea and chlorine *via* Pt(IV), were negative. The experiments were conducted in the same manner as in the work[11].

From the above facts it can be inferred that in Pt(IV) complexes the primary process is the entering of thiourea into the coordination sphere, the oxidation of the ligand being a consecutive process.

The differences in the reactions (A), (B), and (C) can be considered also from the point of view of the different electron donor properties of thiourea and its derivatives. Thiourea is bonded in platinum complexes *via* the sulfur atom[4,21] by a donor σ-bond, and as a consequence the electron density at the central atom increases. This in turn induces secondary charge transfer from the central atom to the free π-orbitals of the ligand. According to the state-of-the-art knowledge, thiourea in the thiol tautomeric form is oxidized most readily, formamidine disulfide resulting as the oxidation product. Derivatives of thiourea the which are unable to exist in the thiol form are more difficult to oxidize. In accordance with this, oxidation to disulfide was found during the reactions with Pt(IV) complex in the case when a derivative of the thiourea is easily converted to the thiol form.

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