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Coordination Complexes of Platinum(II) and Platinum(IV) with Ligands involving the Thioamido Group: Chloro Bridged Mixed-Valence Compounds

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Complexes of the type $[PtL_4][PtCl_6]$ where L = thiourea, thiocaprolactam, tetrahydro-2 pyrimidinethione, 2-imidazolidinethione (ethylenethiourea) and pyrimidine-2 thione, have been synthesized and investigated. This work initiates the study of a new family of mixed valence complexes of platinum involving S-donor ligands.

Introduction

The unusual stoichiometry associated with the platinum complexes of the type PtA_2X_3 or PtA_4X_3 (where A represents ammonia, mono- or diamine, and X halogen or monoanion) have been of interest for some time. The early suggestions regarding the occurrence of Pt(III) in these complexes have been contradicted by X-ray determinations since the first work of Brosset in 1948 devoted to the crystal structure of $Pt(NH_3)_2Br_2 \cdot Pt(NH_3)_2Br_4$ [1]. The crystal structure of these substances consists of infinite chains, with square planar Pt(II) and tetragonal bipyramidal Pt(IV) alternately arranged so as to give ···Pt(II)··· X–Pt(IV)–X chains, the halogen-platinum(IV) bonds being shorter than the platinum(II) ones [2–4]. This formula is further supported by the results of physical properties measurements such as Raman resonance spectroscopy [5–9], magnetic susceptibility, polarized absorption spectroscopy [10] and electrical conductivity measurements [11]. All these data are consistent with 'class II mixed-valence compounds' according to the classification of Robin and Day [12].

In spite of an increasing interest in Pt(II)–Pt(IV) mixed-valence compounds, only a few number of such complexes are known so far. The known examples remain almost entirely limited to species displaying nitrogen donor ligands [13]; in this instance, it is noteworthy that the last described compound is Pt(N-methylimidazole)$_4 \cdot PtCl_6$ [14].

The synthesis and spectroscopic characterization of a Pt(II)–Pt(IV) mixed-valence complex involving thiourea as a ligand have been previously reported [15, 16]. We have then investigated the possibility of extension of this kind of reaction to other ligands belonging either to the thiourea type or to the thiolactam one. In the present paper, compounds of thiocaprolactam (tcp), tetrahydro-pyrimidinethione (ptu), 2-imidazolidinethione (ethylenethiourea, etu), and pyrimidine-2 thione (pyt) are reported.

Experimental Section

Measurements

The X-ray Photoelectron Spectroscopic (XPS) measurements were obtained with an AEI ES 200B spectrometer using MgKα radiation (1253.6 eV) as the X-ray excitation source; the powdered samples were compressed into a copper grid. All spectra were run at a pressure of approximately 5×10^{-8} Torr. The C_{1s} line from oil contamination (B.E. = 285 eV) was used as an internal standard for calibrating the spectra.

XPS spectra were deconvoluted using a program requiring input for the number of peaks and the height, half-width, and position for each peak suspected of comprising the multiplets. Based on these parameters, a spectrum is calculated which can be compared to the experimental spectrum. In all the deconvoluted spectra, we have had a good fit between calculated and experimental spectra. All the spectra were deconvoluted at least twice (for two different runs of the sample). Agreement between two deconvolutions was excellent.

IR spectra were recorded on a Perkin-Elmer Model 577 recording spectrometer using KBr disks; the chloro samples exhibit the same spectra in nujol.

Powder reflectance spectra were obtained with a Cary 14 spectrophotometer at room temperature.

Syntheses

Powdered reagent grade $PtCl_2$, K_2PtCl_4 and crystalline $H_2PtCl_6 \cdot 6H_2O$ were used as starting materials

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TABLE I. Conventional Chemical Analysis Results.

Compound	C, %		H, %		N, %		Pt, %		Cl, %	
	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
$[Pt(etu)_4][PtCl_6]$	14.3	14.5	2.4	2.4	11.1	11.1	38.6	37.2	21.0	21.0
$[Pt(etu)_2Cl_2][Pt(etu)_2Cl_4]$	14.3	14.3	2.4	2.4	11.1	10.7	38.6	38.9	21.0	21.3
$[Pt(ptu)_4][PtCl_6]$	18.0	18.0	2.2	2.3	10.4	10.1	36.0	36.1	26.2	26.0
$[Pt(tcp)_4][PtCl_6]$	25.7	25.8	3.9	4.0	5.0	5.2	34.8	34.0	19.0	18.3
$[Pt(pyt)_4][PtCl_6]$	22.9	22.9	1.9	1.9	5.4	5.3	37.2	37.0	20.3	20.2

for the preparations of the different compounds and solutions. All ligands were of the highest available commercial purity and were used without further purification.

$[PtL_4]Cl_2$ complexes (L = tu, tcp, ptu, etu, pyt)

4 mmol of ligand is dissolved in ethanol (50 ml) and1 mmol of $PtCl_2$ is added. The mixture is then refluxed for two hours with stirring. After filtering to remove any unreacted $PtCl_2$, the solution is reduced to a small volume (20 ml). The resulting precipitate is filtered, washed with diethyl ether and dried *in vacuo*. The physical characteristics of these compounds have been previously described [17–18].

$Pt(Etu)_2Cl_4$

A solution of ethylenethiourea (2 mmol in 20 ml EtOH) is added slowly to an ice-cooled solution of H_2PtCl_6 (1 mmol in 20 ml EtOH). A microcrystalline yellow product immediately separates from the solution. The product is filtered off, washed with EtOH, diethyl ether, and dried *in vacuo* at room temperature. Attempts to prepare the analogous platinum(IV) complexes with the remaining ligands failed.

$[PtL_4][PtCl_6]$ (L = tu, tcp, ptu, etu, pyt)

Method A: If a solution of H_2PtCl_6 in ethanol (10^{-1} *M*) is added dropwise to a solution of the ligand in ethanol (10^{-1} *M*) (molar ratio = 1/3) a microcrystalline colored product immediately separates from the solution. The product is filtered, washed with dry diethylether and dried *in vacuo* at room temperature. *Method B:* $[PtL_4]Cl_2$ (1 mmol) is dissolved in 20 ml of ethanol. $H_2PtCl_6 \cdot 6H_2O$ (1 mmol) in the minimum amount of ethanol is added to this solution. The solution immediately turns orange or red and microcrystalline products precipitate. The product is filtered, washed with dry ethylether and dried *in vacuo*.

$[Pt(etu)_2Cl_2][Pt(etu)_2Cl_4]$

A solution of the ligand in ethanol (0.1 mol) is added to a solution of H_2PtCl_6 in ethanol (0.1 mol) (molar ratio: ligand/Pt = 1/3) and warmed 40 °C under stirring during four hours. The resultant precipitate is filtered, washed with dry ethylether and dried *in vacuo*.

It is noteworthy that in this case, the first step of this reaction is the platinum(IV) complex.

Elemental analytical data for the complexes are given in Table I.

Results and Discussion

Generally speaking, when H_2PtCl_6 and a thioamido entity are allowed to react, species which have to be formulated PtL_2Cl_3 from analytical data are obtained. On the basis of ESCA determinations, these complexes must be considered as Pt(II)·Pt(IV) ones. However, the true nature of these products seem to be dependent on experimental conditions, at least when ethylenethiourea is implied.

When an ethanolic solution of H_2PtCl_6 is added dropwise to an ethanolic solution of the ligand, a $Pt_2L_4Cl_6$ complex separates, the platinum to ligand molar ratio (R) reaching the value 1/3. However, in the thiourea case, a first precipitation is observed when R = 1/6 yielding a $[PtL_4]Cl_2$ complex; with the other ligands, no spontaneous precipitation occurs, but the $[PtL_4]Cl_2$ species may always be precipitated by adding dry ethyl ether to a R = 1/6 mixture. Furthermore, the same $Pt_2L_4Cl_6$ complexes may always be obtained by reacting $[PtL_4]Cl_2$ and H_2PtCl_6 in equimolar amount.

From these data, it can be inferred that the formation of the mixed-valence complex, $Pt_2L_4Cl_6$, involved two steps. The first one, leading to the Pt(II) complex $[PtL_4]Cl_2$, is a reduction of Pt(IV) to Pt(II); this is not unexpected since this step occurs in a reductive medium due to an excess of ligand. Then, $[PtL_4]Cl_2$ reacts with H_2PtCl_6 to yield $Pt_2L_4Cl_6$. According to the scheme previously proposed for the Cu(II) reduction, the redox process operating in the reaction of H_2PtCl_6 with an excess of thioamido ligand may be described by the following equations:

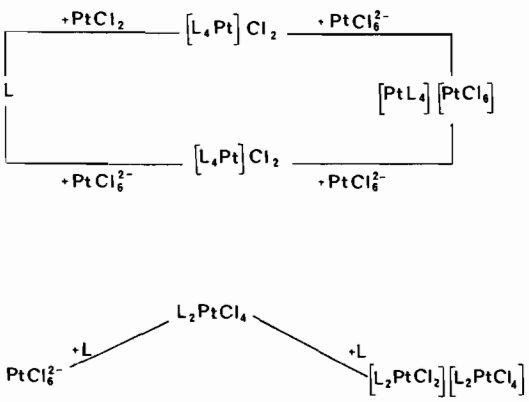


Fig. 1. Diagram illustrating the preparations and the reactions of the complexes described.

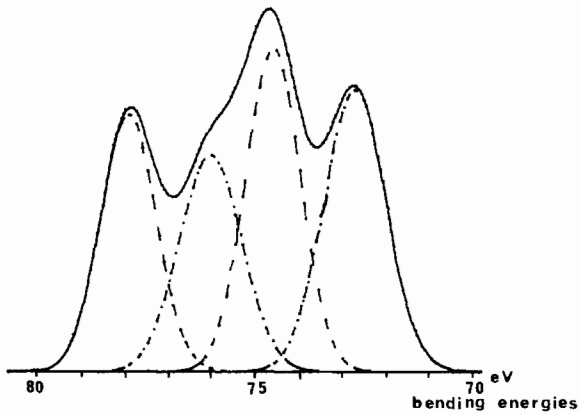


Fig. 2. The platinum 4f region of the X-ray photoelectron spectrum of a mixed-valence compound: (–·–) Pt(II) components, (– – –) Pt(IV) components.

$$6L + H_2PtCl_6 \rightarrow [PtL_4]Cl_2 + 4HCl + 2L' \quad (1a)$$

$$[PtL_4]Cl_2 + H_2PtCl_6 \rightarrow Pt_2L_4Cl_6 + HCl \quad (1b)$$

(L′ represents the reduced form of the ligand).

This reaction sequence strongly suggests that the Pt(II)·Pt(IV) complex has to be formulated $[PtL_4]$-$[PtCl_6]$. It is noteworthy that the reduction of Pt(IV) to Pt(II) (1a) is induced by the five ligands presently studied while it has been reported that ethylenethiourea does not reduce the $[PtCl_6]^{2-}$ ions but leads to a Pt(IV) complex [16].

In fact, such a complex is obtained when the reagents are added in the reverse order. So, if the ligand (ethylenethiourea) is added to H_2PtCl_6 in an alcoholic medium, a precipitation occurs when R = Pt/L is equal to ½. The microanalytical and XPS data show unambiguously that the precipitate is a Pt(IV) complex, PtL_2Cl_4. Further reaction with the ligand in such a manner that R = 1/3 induces the precipitation of a Pt(II)·Pt(IV) complex, Pt_2L_4-Cl_6. These data imply that the reduction process is not the primary step of the reaction.

The whole process may be described here by the following equations:

$$2H_2PtCl_6 + 4L \rightarrow 2PtL_2Cl_4 + 4HCl \quad (2a)$$

$$PtL_2Cl_4 + 2L \rightarrow PtL_2Cl_2 + 2HCl + 2L' \quad (2b)$$

$$PtL_2Cl_2 + PtL_2Cl_4 \rightarrow Pt_2L_4Cl_6 \quad (2c)$$

This reaction Scheme is further supported by considering the possibility of obtaining $Pt_2L_4Cl_6$ by reacting the neutral entities PtL_2Cl_2 and PtL_2-Cl_4, separately prepared, in equimolar amounts. These reactions (Fig. 1) suggest a $[PtL_2Cl_2][PtL_2$-$Cl_4]$ formula for this mixed valence complex.

So, two mixed-valence complexes, $[PtL_4][PtCl_6]$ (A) and $[PtL_2Cl_2]$ $[PtL_2Cl_2][PtL_2Cl_4]$ (B) may be prepared from ethylenethiourea, according to experimental conditions.

Owing to the difficulty of getting monocrystals suitable for X-ray determinations, no direct structural proof can yet be produced; however, the X-ray powder diffraction pattern and the IR spectra of (A) and (B) are markedly different.

As mentioned above, X-ray Photoelectron Spectroscopy has been used in order to obtain more precise information on the different oxidation states of the platinum complexes. To our knowledge, this spectroscopy has not been widely applied to mixed-valence complexes [19, 20] while a lot of studies have been devoted to Pt(0), Pt(II) or Pt(IV) compounds [21, 22].

The data already published assume that the area of the peaks is directly proportional to the number of the elements from which it is derived, and that binding energies $Pt_{4f5/2}$ and $Pt_{4f6/2}$ increase with the oxidation number of the metal, these energies being separated by *ca.* 2 eV in the two oxidation states of the platinum, respectively Pt(II) and Pt(IV).

The Pt_{4f} spectrum of the mixed-valence complexes is a triplet which can be resolved into two doublets of equal intensity (Fig. 2). These two sets of signals are indicative of the presence of Pt(II) and Pt(IV), simultaneously. A shift of 2.1 eV in the $Pt_{4f7/2}$ energy of these products is roughly consistent with two units change in the oxidation state since a shift of 2.3 eV is observed in the case of Wolfram's red salt [19].

It may be emphasized that the spectra reported in Fig. 2 is related to a freshly exposed sample. Furthermore, in contrast to the fact that a $Pt(tu)_2Cl_3$ sample has not suffered any appreciable damage during its exposure to X-rays, when other complexes are subjected to X-ray bombardment, spectral changes indicative of a surface reduction of platinum(IV) to platinum(II) were observed after a few

TABLE II. Binding Energies (±0.2 eV) for the 4f Levels of Platinum.[a]

Compound	$Pt^{IV}_{4f5/2}$	$Pt^{II}_{4f5/2}$	$Pt^{IV}_{4f7/2}$	$Pt^{II}_{4f7/2}$
$[Pt(tu)_4][PtCl_6]$	77.9(1.6)	75.9(1.4)	74.6(1.4)	72.5(1.6)
$[Pt(etu)_4][PtCl_6]$	77.7(1.7)	75.8(1.7)	74.4(1.7)	72.5(1.7)
$[Pt(etu)_2Cl_2][Pt(etu)_2Cl_4]$	77.5(1.6)	75.6(1.5)	74.2(1.5)	72.4(1.6)
$[Pt(ptu)_4][PtCl_6]$	77.7(1.5)	75.8(1.7)	74.3(1.5)	72.4(1.7)
$[Pt(tcp)_4][PtCl_6]$	77.8(1.7)	75.9(1.7)	74.4(1.7)	72.5(1.7)

[a]Fwhm values are given in parentheses (determined by a deconvolution procedure; see text).

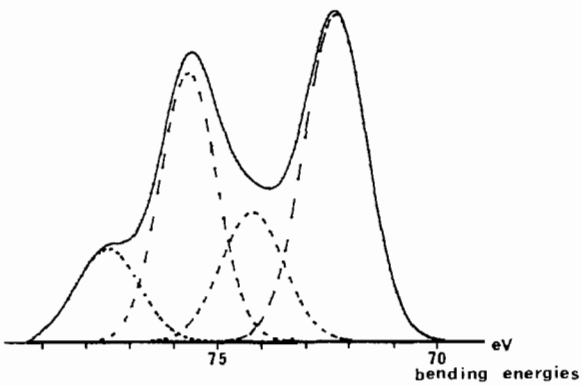


Fig. 3. The platinum 4f region of the X-ray photoelectron spectrum of a mixed-valence compound after about 15 minutes X-ray exposure: (—·—) Pt(IV) components, (— — —) Pt(II) components.

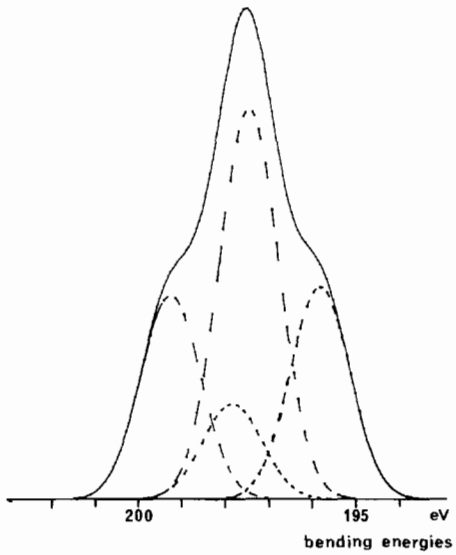


Fig. 4. The Cl_{2p} region of the X-ray photoelectron spectrum of a mixed-valence compound.(-------) calculated peaks assuming the presence of two Cl_{2p} signals.

minutes (Fig. 3). Such X-ray damages of platinum-(IV) compounds have been already reported for mixed-valence and Pt(IV) compounds by Orchard *et al.* [24], Katrib [23] and specially for Wolfram's red salt [19].

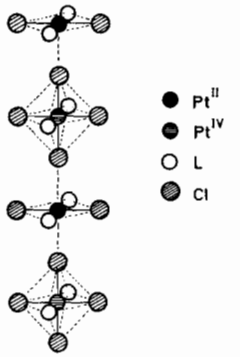
This susceptibility of Pt(IV) to photoreduction is also observed in the $Pt(etu)_2Cl_4$ spectra. On X-ray exposure, Pt(II) signals appear at about 2 eV lower than the Pt(IV) ones.

The Pt(II) and Pt(IV) core electron bending energies for the various complexes are listed in Table II.

It is noteworthy that two sets of signals characteristic of chlorine atoms are also observed in the Cl_{2p} sample spectrum. If the spectrum is recorded immediately after the sample insertion, the ratio of these two lines is close to 2/1. This feature may be related to the fact that in mixed-valence complexes, the axial Pt–Cl bonds are often longer than the equatorial ones [1–3]. In the case of square planar platinum-(II) complexes $(PtLCl_2)_2$, Clark [25] noted a 1 eV difference between terminal and bridging chlorines.

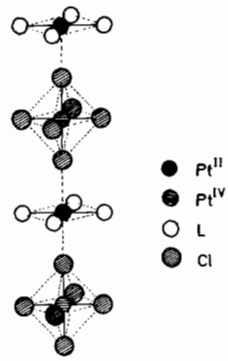
For the present compounds, the calculated spectrum, in the hypothesis of two types of chlorine atoms (axial and equatorial) is shown by the dotted line in Fig. 4. Contrarily to the above-mentioned works, we can also emphasize that the chlorine 2p X-ray photoelectron signal shows significant variations when a Pt(IV) reduction is occurring. Not only the magnitude of the lines decrease, but also the line itself broadens and slightly splits as certainly a result of the formation of Cl_2 or HCl.

According to the last works of Kida [13], the mixed-valence compounds are characterized by an absorption in the visible region, near 500 nm, which would be attributed to a charge transfer transition from Pt(II) to Pt(IV) through the halogen atoms. In the complexes hereabove studied, no clear indication for the occurrence of intervalence charge transfer transitions have been found in the visible spectra, whereas such transitions were observed in thiourea complexes [15]. However, due to problems with insolubility and hydrolytic instability, difficulties were encountered in obtaining single crystals large



$(Pt^{II}L_2Cl_2)(Pt^{IV}L_2Cl_4)$

Fig. 5. The skeletal structure of $[PtL_2Cl_2][PtL_2Cl_4]$ mixed-valence complex.



$(Pt^{II}L_4)(Pt^{IV}Cl_6)$

Fig. 6. The skeletal structure of $[PtL_4][PtCl_6]$ mixed-valence complex.

enough and the reflectance spectra have been obtained from a microcrystalline powder.

While the platinum oxidation states of these compounds seem to be well established, the nature of the coordination sites still remains to be defined.

Regarding the ligand part of the IR spectra of the mixed-valence complexes, it closely corresponds to their $[PtL_4]Cl_2$ homologs for which coordination through the sulfur atom has been well inferred [18]; furthermore, this type of coordination has been definitively established by an X-ray determination of the structure of the $[Pt(tu)_4)]Cl_2$ complex [26].

As for the complexes of ethylenethiourea, the observation of two ν(Pt–Cl) bands for $[Pt(etu)_2Cl_2][Pt(etu)_2Cl_4]$, respectively obtained at 325 and 310 cm^{-1}, can be explained by a composite of $Pt(etu)_2Cl_2$ (310,s; 320,sh) and of $Pt(etu)_2Cl_4$ (315,sh; 325,s). In contrast, for the $[Pt(etu)_4][PtCl_6]$ complex, the ν(Pt–Cl) bands are shifted towards the higher frequencies, *i.e.* 320 and 325 cm^{-1}, respectively.

Furthermore, it appears that the X-ray powder diffraction patterns of these two compounds are very different; therefore, we can conclude that the $Pt_2(etu)_4Cl_6$ complexes exist under two different forms: either $[Pt(etu)_4][PtCl_6]$ or $[Pt(etu)_2Cl_2][Pt(etu)_2Cl_4]$. The latter assumption is further supported by the isolation of intermediate compounds during the course of their synthesis.

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