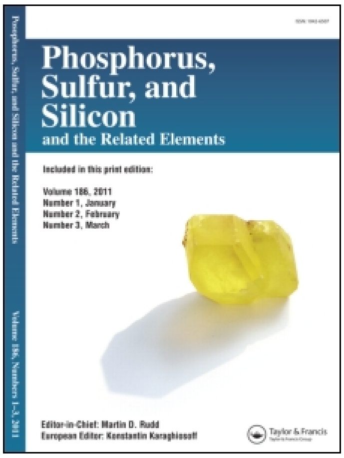

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REDUCTIVE PROPERTIES OF THIOAMIDES IN COMPLEX FORMATION MIXED-VALENCE COMPLEXES OF PLATINUM FROM THIOHYDANTOIN

Philippe Arrizabalaga[a]; Paule Castan[a]; Enrique Colacio-rodriguez[b]
[a] Laboratoire de Chimie de Coordination du CNRS, associé á I'Université Paul Sabatier 205, Toulouse, France [b] Departmento de Quimica Inorganica, Facultad de Ciencias, Granada, Spain

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REDUCTIVE PROPERTIES OF THIOAMIDES IN COMPLEX FORMATION MIXED-VALENCE COMPLEXES OF PLATINUM FROM THIOHYDANTOIN

PHILIPPE ARRIZABALAGA and PAULE CASTAN*
Laboratoire de Chimie de Coordination du CNRS, associé à l'Université Paul Sabatier 205, route de Narbonne, 314000 Toulouse, France

and

ENRIQUE COLACIO-RODRIGUEZ
Departmento de Quimica Inorganica, Facultad de Ciencias, Granada, Spain

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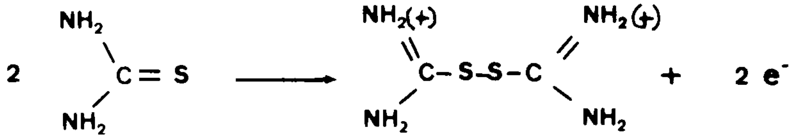
Mixed valence complexes have been obtained using in a one pot synthesis the complexing and reducing properties of thiohydantoin (ThH). Two complexes, i.e. $[Pt(ThH)_4][PtCl_6]$ and $[Pt(Th)_2][Pt(ThH)_2Cl_4]$ have been obtained. These complexes having platinum atoms in two different oxidation states and bridged by halogen atoms are compared in view of their conductive properties to the classical class II mixed valence complexes such as Wolffram's red salt.

INTRODUCTION

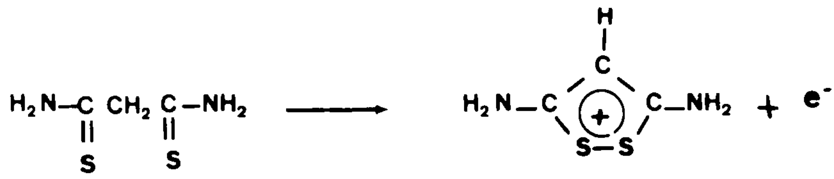
Since the first work of Baggesgaard Rasmussen, the salient properties of thioamides and thioureas have been underlined.[1] A number of their reactions may readily be explained by assuming that a thioamide reacts in its thiol form:

$$-\underset{\underset{S}{\parallel}}{C}-NH_2 \rightleftharpoons -\underset{\underset{SH}{|}}{C}=NH$$

Then, they are expected to be oxidized to disulfides. Such oxidation can be obtained either electrochemically or with a number of oxidants. For example, thiorea gives the dithiobis(formamidinium) ion.



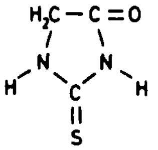
It may be underlined that the oxidation process is often more complex, e.g.:[2,3]



It is known that platinum metals have a strong tendency to form complexes with sulfur-containing ligands. The complex compounds of these metals with thioamides have been extensively studied. They are of great interest both theoretically and practically. Since the last century Kurnakov,[4] then Chernyaev[5] hav afforded a major contribution to the knowledge of substitution reactions in square planar complexes with a particular reference to the trans effect of these ligands. Further, numerous methods of collective and selective isolation of platinum metals by means of thioamide complexes have been developed and introduced in the industry.

With metals in high oxidation states, thioamides, thiourea and their derivatives react not only as complexing agents but also as reductants. Complexes of metals in low oxidation state have been isolated for copper (II to I),[6,7] osmium (VII to III),[8] and some other metals.[9] Thus, platinum(IV) may be titrated by thiourea.[10] In this case, the molar ratio of Pt(IV) to the titrant at the end point is 1:6, indicating that Pt(IV) is reduced to Pt(II) with subsequent formation of a $[Pt(thiourea)_4]^{2+}$ complex.

Recently, we have shown that this reaction proceeds stepwise and that, under careful conditions, stabilization of platinum in its higher oxidation state may be obtained in a mixed-valence arrangement involving linear arrays of alternating square planar Pt(II) and octahedral Pt(IV) entities.[11] In this paper, we report some findings on the reaction of thiohydantoin (Figure 1) with platinum(IV) yielding either platinum(II) compounds or mixed-valence Pt(II)–Pt(IV) compounds.



RESULTS AND DISCUSSION

Thiohydantoin† has been used as ligand with a variety of transition metals.[12,13] It is actually a very interesting ligand since both amide and thioamide moieties are present in one molecule, offering four potential coordination sites. In all the complexes previously obtained, thiohydantoin acts as monodentate either through sulfur or through oxygen, but we have recently shown that with platinum(II) this ligand may also act as a chelating agent coordinated to the metal through their sulfur atom and one of the two nitrogen atoms.[14]

With this in mind, it may be interesting to investigate the three possibilities of thiohydantoin towards platinum(IV), i.e. its complexing, chelating and reductive behavior.

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† In the course of this paper, thiohydantoin will be abbreviated as ThH while its deprotonated form is Th.

Compound A

We have shown earlier[11] that, when H_2PtCl_6 and a thioamido entity are allowed to react, species are obtained that are formulated as PtL_2Cl_3 from analytical data. On the basis of XPS determination, these complexes must be considered as Pt(II)–Pt(IV) species. This is also the case for complex A, whose analytical, NMR and XPS data are in good agreement with such a formula.

The XPS Pt_{4f} spectrum is a triplet that can be deconvoluted into two doublets of equal intensity indicative of the simultaneous presence of Pt(II) and Pt(IV). The relevant binding energies for the Pt_{4f} levels of platinum are respectively 77.8 and 74.5 eV for Pt(IV), and 75.8 and 75.2 for Pt(II). These values, as well as the shift of ca. 2 eV between the two $Pt_{4f7/2}$ energies, fit well those obtained for other thioamido mixed-valence complexes[11] or amino mixed-valence compounds.[15] Moreover, the ^{195}Pt NMR spectrum is straightforward since it is the sum of the spectra relating to the isolated entities, $[Pt(ThH)_4]^{2+}$ and $[PtCl_6]^{2-}$, i.e. two lines at +430 $(PtCl_6)^{2-}$ and −3917 ppm, respectively. The ^{13}C ($\underline{C}$=S) spectra exhibit only one signal at 184.0 ppm. This very poor high field shift of the $\underline{C}$=S signal (183.5 ppm for the free ligand) is indicative of a thioamido entity coordinated on a platinum(II).

Finally, both ^{195}Pt and ^{13}C spectra are strictly identical to those of compound B obtained upon mixing H_2PtCl_6 and $[Pt(ThH)_4]Cl_2$. Compounds A and B may be formulated as $[Pt(ThH)_4][PtCl_6]$. The preparative scheme proposed for this complex involves two steps. The first step is a reduction process of Pt(IV) to Pt(II) occurring in a reductive medium due to an excess of ligand.

$$6\,ThH + H_2PtCl_6 \xrightarrow{\text{reduc.}} [Pt(ThH)_4]Cl_2 + Th\text{–}Th + 4\,HCl$$

$[Pt(ThH)_4]Cl_2$ then reacts with H_2PtCl_6 to yield the mixed-valence complex:

$$[Pt(ThH)_4]Cl_2 + H_2PtCl_6 \longrightarrow [Pt(ThH)_4][PtCl_6] + 2HCl$$

This compound is also obtained directly, as described in (B).

Compound C

Compound C requires a more thorough study as the formula inferred from analysis, $Pt(ThH)_2Cl_2$, allows an oxidation state of II for the metal since the complexation is accompanied by the complete reduction of the metal. Actually, the complexity of the NMR spectra does not allow to consider this hypothesis. Moreover, in this case also, the XPS spectra exhibit two doublets of equal intensity in the Pt_{4f} spectrum. The relevant binding energies for the $4f$ levels of platinum are 77.5 and 74.2 eV for Pt(IV), and 75.2 and 72.0 eV for Pt(II). The shift of ca. 2 eV in the Pt_{4f} energy of these products is roughly consistent with a two-unit change in the oxidation state of the metal.[17] In view of the XPS spectra, compound C must be considered as a mixed-valence complex. This is relevant with the ^{13}C spectra which exhibit two ($\underline{C}$=S) signals at 176.6 and 156.2 ppm. When comparing the two $\delta\underline{C}$=S changes with the same ligand, the more pronounced shielding, consistent with a lowering of the C=S bond order, may be related to the increase of the σ donor ability of sulfur toward platinum(IV) with respect to platinum(II). Many other ligands such as phosphine or CN^{-18} are also capable of varying their net balance of donor behavior toward other metal atoms. More often, it is the electron density on the ligands and not on the metal that differs. This is relevant with the ^{195}Pt spectra which exhibit two neighbouring signals at −3750 and −3920 ppm, respectively. It may be underlined that for the C compound the reagents are added in the reverse order than for the compound A, i.e. thiohydantoin added to H_2PtCl_6, so the begining of the reaction involves a lack of ligand towards the metal and we may presume that the platinum(IV) complex $Pt(ThH)_2Cl_4$ is obtained as a first step.

$$H_2PtCl_6 + 2\,ThH \longrightarrow Pt(ThH)_2Cl_4 + 2\,HCl$$

This complex is readily reduced (with subsequent elimination of HCl) to the platinum(II) complex $Pt(ThH)_2Cl_2$.

$$Pt(ThH)_2Cl_4 + 2\,ThH \xrightarrow{reduc.} Pt(ThH)_2Cl_2 + Th\text{\_}Th$$

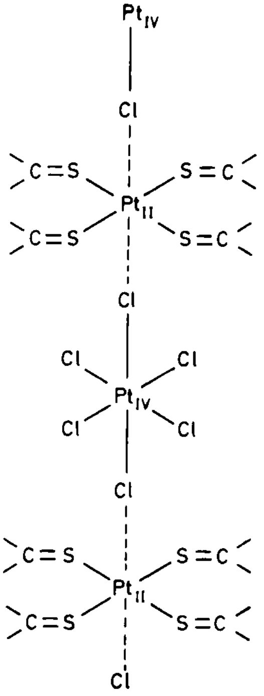
In fact we have recently shown[14] that the complex $Pt(ThH)_2Cl_2$ is not stable and that the $Pt(Th)_2$ complex may be readily obtained, complex in which thiohydantoin acts as chelating agent toward platinum coordinated to the metal through their sulfur and one of the deprotonated nitrogen.

$$Pt(ThH)_2Cl_2 \longrightarrow Pt(Th)_2 + 2\,HCl$$

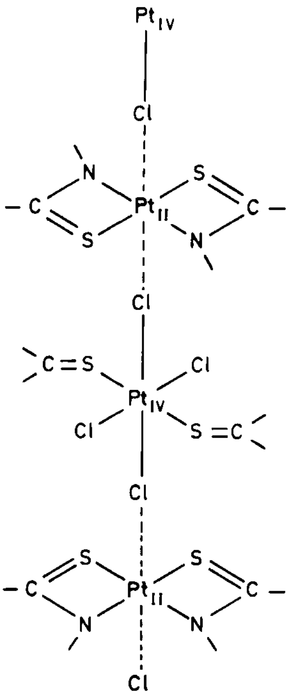
The reaction of the two entities, $Pt_{II}(Th)_2$ and $Pt_{IV}(ThH)_2Cl_4$ produces an almost insoluble mixed-valence complex $[Pt(Th)_2][Pt(ThH)_2Cl_4]$. An excess of ligand, however low it may be, involves the partial or total redissolution of the mixed-valence complex with subsequent formation of a platinum(II) complex.

Complexes having platinum atoms in two different oxidation states and bridged by halogen atoms known as Wolffram's Salt analogues present the basic structure of linear chain of halide bridged alternating Pt(II) and Pt(IV) (Figure 2) which are surrounded by four donor atoms in the plane perpendicular to the chain direction. Additional evidences for electronic interactions within the chains has been obtained from electrical conductivity measurements.[19–21] Since no sufficiently large single crystals were available here, powder conductivity measurements were determined on compressed pellets and the conductivity averaged over all directions of the crystals. The values obtained i.e. $4.45 \times 10^{-8}\,\Omega^{-}.\,cm^{-1}$ for the compound A and $1.45 \times 10^{-7}\,\Omega^{-}.\,cm^{-1}$ for the compound C compared well with those obtained for amino-platinum class II mixed-valence complexes belonging to the Wolffram's red salt family.[22]

In the course of the work the various properties of thiohydantoin as reductant, complexing and chelating agent has been used to obtain mixed valence complexes i.e. $[Pt(ThH)_4][PtCl_6]$ (A) and $[Pt(Th)_2]$ $[Pt(ThH)_2Cl_4]$ (C). We have already obtained type (A) compounds by one pot reaction using various thioamides or thiourea compounds,[11] however in compound (C) the ligand may react as a chelating agent coordinated to Pt(II) by one sulphur and one nitroyen atom by loss of a proton.



Complex A



Complex C

Although thiohydantion was a strong reductant, metal–metal interaction occuring through chlorine in the mixed-valence complex thus stabilizes the higher oxidation state of the platinum.

EXPERIMENTAL

IR spectra were recorded on a Perkin–Elmer Model 577 spectrometer using KBr disks; the chloro complexes exhibit the same spectra in Nujol.

The X-ray photoelectron spectroscopic (XPS) measurements were obtained with an AEI ES 200B spectrometer using Mg Kα radiation (1253.6 eV) for excitation; 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 calibration.

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

All NMR spectra were recorded on a WH250 Bruker spectrometer operating in the Fourier transform mode and equipped with wide band probe (23–103 MHz).

The complexes were dissolved in DMSO-d_6, the ^{2}H resonance of which provided the field/frequency locking signal. ^{1}H noise modulated decoupling ensured complex proton decoupling of the spectra.

^{13}*C spectra*

Typical parameters for ^{13}C spectra were: pulse width 20 μsec, impulse delay 1 sec; 2000–5000 accumulations were usually necessary to achieve a satisfactory signal to noise ratio. The ^{13}C shifts were measured relative to the solvent DMSO-d_6, however, δ values reported are quoted with respect to TMS.

^{195}*Pt spectra*

Typical parameters for ^{195}Pt spectra were: pulse width 20 μsec, impulse delay 1 sec; 500–3000 transients were collected. All the previous papers reporting ^{195}Pt chemical shifts mention use of different compounds as the reference zero. We have adopted the convection suggested by Kerrisson,[23] which conforms to that of the IUPAC using ^{195}Pt of H_2PtCl_6 in D_2O solution as external zero reference at 53 770 768 MHz. The dependence of the chemical shift of the solvent was examined in the case of H_2PtCl_6 by use of solutions in DMSO-d_6.

Solutions for NMR spectra were nearly saturated and data were collected on freshly prepared samples. The data given were quite reproducible and there was no evidence of solvolysis or decomposition of the complexes during the course of the measurements.

A positive shift implies that the sample resonance occurs at a higher frequency and that the ^{195}Pt nucleus is less shielded than in reference.

Preparation of the complexes

$Pt(ThH)_4Cl_2$. This was prepared following Dini's method.[24] $PtCl_2$ (0.5 mmol) was added to the ligand (4 mmol) dissolved in EtOH (50 cm). The mixture was heated under reflux with stirring for two hours. After filtering, the solution was reduced to 20 cm. The resulting precipitate was filtered off, washed with EtOH and Et_2O, and dried in vacuo.

$Pt(Th)_2{\cdot}2H_2O$. This compound was prepared as previously described.[14]

Mixed-valence complexes. Complex A: 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) (platinum to ligand molar ratio: 1:3). A microcrystalline red product immediately separates from the solution. The product is filtered off, washed with dry ethylether and dried in vacuo at room temperature.

Elemental analytical data for $Pt_2C_{12}H_{16}Cl_6N_8O_4S_4$. Calculated: Pt, 36.55; C, 13.50; H, 1.50; N, 10.50; Cl, 19.96. Found: Pt, 35.60; C, 13.81; H, 1.70; N, 10.42; Cl, 19.58.

Complex B: $[PtL_4]Cl_2$ (1 mmol) is dissolved in water. $H_2PtCl_6{\cdot}6H_2O$ (1 mmol) in the minimum amount of water is added to this solution. The solution immediately turns strong red and a microcrystalline product precipitates.

Elemental analytical data for $Pt_2C_{12}H_{16}Cl_6N_8O_4S_4$. Calculated: Pt, 36.55; C, 13.50; H, 1.50; N, 10.50. Found: Pt, 36.22; C, 13.27; H, 1.47; N, 10.46.

Complex C: a solution of the ligand in ethanol is added to a solution of H_2PtCl_6 in ethanol (ligand to Pt molar ratio: 1:6) and warmed (40°C) upon stirring for one hour. The resultant red brown precipitate is filtered off, washed with dry ethylether and dried in vacuo.

Elemental analytical data. Found: Pt, 38.7; C, 14.38; H, 1.58; N, 11.14.

Analytical data performed for the three compounds allow the following formulation: $Pt(ThH)_2Cl_3$ for compounds A and B, $Pt(ThH)_2Cl_2$ for compound C, this proposed formula may be refined especially in view of NMR and XPS results (vide supra).

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