Inorganica Chimica Acta, 54 (1981) L237–L238
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

Bromo Bridged Mixed-Valence Complexes of Platinum with Thioamido Ligands

JEAN-MICHEL BRET, PAULE CASTAN* and JEAN-PIERRE LAURENT

Laboratoire de Chimie de Coordination du CNRS associé à l'Université Paul Sabatier, 205 route de Narbonne, 31400 Toulouse, France

Received May 7, 1981

Complexes of the type PtA_nX_3 (A = monodentate or bidentate neutral aminoligand, X = halogen and n = 1 or 2) have been well known for many years [1–5]. The structural studies and the results of physical measurements are consistent with 'class II mixed-valence compounds' according to the classification of Robin and Day [6]. Despite the large number of compounds which have been reported today the known examples remain almost entirely limited to species displaying nitrogen donor ligands.

In the course of our investigations on a new family of mixed-valence compounds involving S-donor ligands (L), we have already described some chloro bridged complexes of general formula PtL_2Cl_3 [7–8]. The present work is devoted to complexes originating from the interaction of H_2PtBr_6 with the reactive –NH–C=S– group to give bromo bridged mixed valence complexes of platinum. In this paper compounds of thiocaprolactam (tcp), tetrahydro-pyrimidinethione (ptu), 2-imidazolidinethione (ethylenethiourea, etu), pyrimidine-2 thione (pyt) and thiourea (tu) are considered.

As previously reported [8], the reaction between H_2PtCl_6 and a thioamido compound (L) leads to the isolation of a $Pt_2L_4Cl_6$ species when the platinum to ligand molar ratio reaches the value 1/3. However the course of the $Pt_2L_4Cl_6$ complex seems to be dependent on experimental conditions at least when ethylenethiourea is involved. The same general behaviour is observed when H_2PtCl_6 is replaced by H_2PtBr_6. Generally speaking a 1/3 reaction mixture affords a species which has to be formulated PtL_2Br_3 from analytical data but the crude formulation applies to two complexes, *i.e.* $[PtL_4][PtBr_6]$ and $[PtL_2Br_2][PtL_2Br_4]$.

$[PtL_4][PtBr_6]$ Complexes

If H_2PtBr_6 is added to the ligand, a complex precipitates as soon as the required stoichiometry (1/3) is reached. However, in the thiourea case, a first precipitation is observed when the platinum to ligand molar ratio reaching the value 1/6, this compound is a $(PtL_4)Br_2$ complex; with the other ligands, no spontaneous precipitation occurs, but the platinum(II) species can always be precipitated by adding dry ethyl ether to a 1/6 mixture. Furthermore, species $Pt_2L_4Br_6$, displaying the same characteristics (i.r. and X-ray powder spectra) is obtained by reacting the platinum(II) complex $(PtL_4)Br_2$ with H_2PtBr_6.

These data suggest the following scheme:

$$6L + H_2PtBr_6 \rightarrow (PtL_4)Br_2 \qquad \text{(reduction Pt(IV) to Pt(II))}$$

$$(PtL_4)Br_2 + H_2PtBr_6 \rightarrow [PtL_4][PtBr_6]$$

$[PtL_2Br_2][PtL_2Br_4]$ Complexes

If the ligand is poured onto H_2PtBr_6, precipitation occurs only after the 1/3 mixture has been warmed to 40 °C and stirred for four hours. An intermediate species has been isolated when L is ethylenethiourea. This is a platinum(IV) complex, PtL_2Br_4, which, on reacting further with the ligand, yields the expected product $Pt_2L_4Br_6$.

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

$$2H_2PtBr_6 + 4L \rightarrow 2PtL_2Br_4$$

$$PtL_2Br_4 + 2L \rightarrow PtL_2Br_2$$

$$PtL_2Br_4 + PtL_2Br_2 \rightarrow [PtL_2Br_2][PtL_2Br_4]$$

The new compounds are listed in Table I, together with their analytical data and their assigned Metal–Br stretching frequencies.

The infrared spectra show the absorptions due to ligand vibrations [9]. On complexation either with Pt(II) or with Pt(IV) the ligand absorptions show the typical alterations which may be attributed to sulfur coordination, *i.e.* the shift to higher frequencies of the broad absorption band in the 1400–1600 cm^{-1} range indicating an increase in the double bond character of the CN link.

The Pt–Br stretching frequencies can easily be assigned because of their high intensity. No attempts have been made to assign Pt–ligand vibrations since an unambiguous assignment is very difficult.

---

*Author to whom correspondence should be addressed.

TABLE I. Analytical and I.R. Data of the New Compounds.[a]

Compounds	C %	H %	N %	Pt %	Br %	ν(Pt–Br) cm^{-1}
$[Pt(tu)_4]Br_2$	7.27	2.42	–	26.72	25.20	
	(7.28)	(2.42)	(16.99)	(29.59)	(24.28)	
$Pt(etu)_2Br_4$	9.98	1.73	8.23	27.43	45.12	220, 225sh
	(10.01)	(1.67)	(7.79)	(27.12)	(44.50)	
$[Pt(tu)_4][PtBr_6]$	3.90	1.34	–	32.99	40.11	223, 230
	(4.06)	(1.35)	(9.47)	(32.99)	(40.60)	
$[Pt(etu)_4][PtBr_6]$	10.67	1.85	–	30.60	37.36	225sh, 230
	(11.28)	(1.87)	(8.76)	(30.52)	(37.56)	
$[Pt(etu)_2Br_2][Pt(etu)_2Br_4]$	10.35	1.73	8.43	29.40	37.73	220, 225sh
	(11.28)	(1.87)	(8.76)	(30.52)	(37.56)	
$[Pt(ptu)_4][PtBr_6]$	13.86	2.33	8.53	29.63	35.92	225, 230sh
	(14.38)	(2.39)	(8.39)	(29.22)	(35.96)	
$[Pt(ptu)_2Br_2][Pt(ptu)_2Br_4]$	14.38	2.37	8.78	29.68	35.84	220, 227sh
	(14.38)	(2.39)	(8.39)	(29.22)	(35.96)	
$[Pt(tcp)_4][PtBr_6]$	21.53	3.17	3.78	28.14	32.88	225, 230sh
	(20.76)	(3.11)	(4.03)	(28.11)	(34.61)	
$[Pt(tcp)_2Br_2][Pt(tcp)_2Br_4]$	20.26	3.10	4.05	28.34	35.00	220sh, 225
	(20.76)	(3.11)	(4.03)	(28.11)	(34.61)	
$[Pt(pyr)_2Br_2][Pt(pyr)_2Br_4]$	18.27	1.53	–	30.07	36.56	225
	(18.26)	(1.52)	–	(29.68)	(36.56)	

[a] Calculated values in parentheses.

It may be emphasised that for all the ligands but thiourea both isomers, *i.e.* $[PtL_4][PtBr_6]$ and $[PtL_2Br_2][PtL_2Br_4]$ have been obtained while only one $[PtL_2Cl_2][PtL_2Cl_4]$ (L = ethylenethiourea) has been prepared. This is in agreement with the strong 'b character' of platinum for which the stability of the halide complexes decreases on going from the bromo to the chloro species. Owing to the difficulty of getting monocrystals suitable for X-ray determinations, no direct structural proof can be produced yet to affirm that we have two different isomers; however, the intermediate products isolated and the powder diffraction patterns of the two mixed-valence species are markedly different.

Experimental

All spectral measurements were carried out by the methods given earlier [7, 8].

$[(tu)_4Pt]Br_2$

Four millimol of ligand are dissolved in ethanol (50 ml) and one millimol of K_2PtBr_4 is added. The mixture is then refluxed. The resulting precipitate is filtered, washed with diethyl ether and dried *in vacuo*.

$[PtL_4][PtBr_6]$ (L = tu, etu, ptu, tcp)

Method A: Single step synthesis

A solution of H_2PtBr_6 in ethanol (10^{-1} *M*) is added dropwise to a solution of the ligand in ethanol (10^{-1} *M*) (molar ratio Platinum/ligand = 1/3). The microcrystalline colored product immediately separates from the solution. The product is filtered, washed with dry ethyl ether and dried *in vacuo* at room temperature.

Method B

$[PtL_4]Cl_2$ (10^{-3} *M*) is dissolved in the minimum amount of water, and 2 g of KBr are added. H_2PtBr_6 (10^{-3} *M*) is then added to this solution. The mixed valence compound precipitates immediately and is next filtered, washed with water, ethanol and dry ethyl ether and dried *in vacuo* at room temperature.

$[PtL_2Br_2][PtL_2Br_4]$ (L = etu, ptu, tcp, pyt.)

A solution of the ligand in ethanol (10^{-1} *M*) is added to a solution of H_2PtBr_6 in ethanol (10^{-1} *M*) (molar ratio ligand/Pt = 3/1) and warmed to 40 °C under stirring during four hours. The resultant precipitate is filtered, washed with dry ethyl ether and dried *in vacuo.*

References

1 C. Brosset, *Arkiv. Kemi, Mineral. Geol., 25A,* 19 (1948).
2 B. M. Craven and D. Hall, *Acta Cryst., 14,* 475 (1961).
3 J. Wallen, C. Brosset and N. Vannerberg, *Arkiv. Kemi, 18,* 541 (1961).
4 B. M. Craven and D. Hall, *Acta Cryst., 21,* 177 (1966).
5 N. Matsumoto, M. Yamashita and S. Kida, *Bull. Chem. Soc. Japan, 51,* 2334 (1978).
6 M. B. Robin and P. Day, *Adv. Inorg. Chem. Radiochem., 10,* 247 (1967).
7 P. Arrizabalaga, P. Castan and J. P. Laurent, *Chem. Phys. Letters, 76,* 548 (1980).
8 J. M. Bret, P. Castan and J. P. Laurent, *Inorg. Chim. Acta,* to be published.
9 P. Castan and J. P. Laurent, *Trans. Metal. Chem., 5,* 154 (1980).