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Halogen-Bridged Complexes of Platinum with Alkylsulphoxides

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Introduction

Dimethylsulphoxide (DMSO) complexes of platinum(II) have been prepared by Kukushkin *et al.* [1]. These authors attempted without success to prepare the iodo analogues by mixing a solution of potassium tetraiodoplatinate with DMSO. However, under similar conditions, or by mixing KI and K[Pt(DMSO)Cl_3] in aqueous solution, we isolated a red-brown precipitate which analyzed correctly for the formula [Pt(DMSO)I_2]$_2$. The complex can be recrystallized from hot DMSO without decomposition. We therefore decided to study this kind of complex in detail. In this paper, we report the I, Cl and Br analogues of DMSO and the I analogues of diethyl (DESO), di(n-propyl) (DPSO), di(n-butyl) (DBSO) and tetramethylene (TMSO) sulphoxide platinum complexes.

Experimental

K[Pt(DMSO)X_3] (X = Cl and Br) [1, 2] and *cis*-[Pt(TMSO)$_2Cl_2$] [3] were prepared according to the methods described in the literature.

[Pt(L)I$_2$]$_2$ (L = DMSO, DESO, DPSO and DBSO)

A K_2PtI_4 solution was obtained by mixing K_2PtCl_4 (0.415 g in 5 ml H_2O) and KI (0.67 g in 5 ml H_2O) for five minutes. 1 mmol of L was then added to the K_2PtI_4 solution and a precipitate appeared immediately. After 30 minutes, the precipitate was filtered off, washed with water and dried under vacuum in the presence of $CaCl_2$. The compound was purified by dissolving in chloroform (hot for L = DMSO) and filtered if not clear. The $CHCl_3$ solution was evaporated to dryness and the compound was washed with n-hexane and air dried. Yield: 85%.

[Pt(TMSO)I$_2$]$_2$

1 mmol of *cis*-[Pt(TMSO)$_2Cl_2$] and 0.34 g of KI were mixed in 5 ml of water. The suspension was stirred for 3 hours. The red-brown precipitate was then filtered off and washed with water and dried under vacuum in the presence of $CaCl_2$. The compound was finally purified with chloroform as the above compound. Yield: 65%.

[Pt(DMSO)X$_2$]$_2$ (X = Cl and Br)

K[Pt(DMSO)X_3] and $AgNO_3$ were mixed in water in 1:1 molar ratio at 50 °C. After 3 hours, AgCl was filtered off and the filtrate was evaporated to dryness at 40 °C. The product was separated from KNO_3 by dissolving in $CHCl_3$ (hot for X = Cl) and filtering. The $CHCl_3$ filtrate was evaporated to dryness and the product was washed with ether. Yield: 80%.

[Pt(DMSO)(L)Cl$_2$] (L = CH$_3$CN, DMF)

[Pt(DMSO)Cl_2] was dissolved in $CHCl_3$ and an excess of L (5X) was added. After 30 minutes, the solution was evaporated to dryness and the residue was washed with ether. The product is obtained in a quantitative yield.

Elemental analyses were done by Chemalytics Inc. and molecular weights were measured by Galbraith Inc.

Results and Discussion

The structure of the bridged iodo-compounds, [Pt(L)I_2]$_2$, was assigned by analytical data, molecular weight measurements and the fact that platinum(II) has a square planar coordination. The molecular weights were measured in chloroform, dimethylformamide (DMF) and benzene (Table I). Compounds of DESO, DPSO and DBSO in chloroform showed a molecular weight fairly close to that of the dimer. The DMSO compound in DMF is not a dimer because DMF can cleave the bridged bond to form the solvated compound [Pt(DMF)(DMSO)I_2]. The molecular weight of the DBSO compound in benzene is much higher than that of the dimer. It seems that molecular associations exist more or less in non-polar solvents.

All the iodo compounds do not react further with sulphoxides, *i.e.*, [Pt(L)$_2I_2$] cannot be prepared from the reaction of K_2PtI_4 or [Pt(L)I_2]$_2$ and an excess of L. Displacement of the chloro ligands from [Pt(L)$_2Cl_2$] with KI causes one L to leave and the dimer [Pt(L)I_2]$_2$ is formed. Compounds of the cyclic sulphoxide, TMSO, show different properties towards KI. [Pt(TMSO)I_2]$_2$ reacts with KI to form K[Pt(TMSO)I_3] which is very soluble in water and can be precipitated out by adding $(C_2H_5)_4NCl$. The compounds of the n-alkyl sulphoxides, DMSO, DESO, DPSO and DBSO are quite inert to KI.

Pyridine (py) reacts with [Pt(L)I_2]$_2$ to form *trans*-[Pt(L)(py)I_2] which is quite different from its chloro-analogue. For example, *trans*-[Pt(DMSO)(py)I_2] loses pyridine gradually in DMSO solution, while *trans*-[Pt(DMSO)(py)Cl_2] can be recrystallized without loss of pyridine [4].

The chloro and bromo-bridged complexes [Pt(DMSO)X_2]$_2$ were made from K[Pt(DMSO)X_3] and

TABLE I. Elemental Analysis, Melting Point and Molecular Weight.[a]

Compound	C	H	X	S	M.p.	M.W. (Solvent)
$[Pt(DMSO)I_2]_2$	4.55	1.14	48.20	6.02		1054
	4.72	1.15	46.33		190	425(DMF)
	4.66	1.01				
$[Pt(NBSO)I_2]_2$	15.16	2.47	41.85			1222
						1004($CHCl_3$)
	15.87	2.81	41.40			1534(C_6H_6)
$[Pt(DMSO)Br_2]_2$	5.50	1.40	37.00	7.40		
	6.43	1.19	36.00	7.06	215	
$[Pt(DMSO)Cl_2]_2$	6.98	1.76	20.60			
	7.20	1.57	20.59		215	
$Pt(DMSO)(CH_3CN)Cl_2$	12.47	2.35	18.42			
	11.90	2.08	18.24		185	
$[Pt(DESO)I_2]$	8.65	1.80	45.77	5.77	170	1110
	8.76	1.68				846($CHCl_3$)
$[Pt(DPSO)I_2]$	12.35	2.40	43.57	5.49		1166
	12.90	2.30			200	928($CHCl_3$)

[a] Calculated value in first row.

$AgNO_3$. The bridged bonds can be easily cleaved by DMSO, CH_3CN, DMF and KX to form $[Pt(DMSO)_2X_2]$, $[Pt(DMSO)(CH_3CN)X_2]$, $[Pt(DMSO)(DMF)X_2]$ and $K[Pt(DMSO)X_3]$ respectively, while the iodo compound is inert to these reagents. $[Pt(DMSO)(CH_3CN)X_2]$ is very stable, but $[Pt(DMSO)(DMF)X_2]$ loses DMF under vacuum.

The infrared and N.M.R. data of these complexes indicate that the sulphoxide ligands are bonded to platinum through the sulphur atom [5], CH_3CN through the nitrogen atom [6] and the DMF molecule through oxygen [7].

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