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Trans Platinum(II) Complexes with Pyridine and Substituted Pyridines

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Complexes of the type trans-PtL_2X_2 *(L = pyridine, 2-picoline, 3-picoline, 4-picoline and 3,5-lutidine; X = Cl, Br, NCS) have been synthesized by nucleophilic displacement of two ligands from the tetrakis ion* $[Pt(L)_4]^{2+}$ *by the appropriate anion X, either in the solid state or in aqueous solution. Thermal degradation of the solid tetrakis complexes* $[Pt(L)_4]\cdot X_2$ *(L = 4-picoline, 3,5-lutidine, X = Cl, Br, NCS) and* $[Pt(3\text{-picoline})_4]X_2$ *(X = Cl, Br) led to the appropriate* trans-*complex* PtL_2X_2. *In the other cases nucleophilic displacement by the appropriate anion occurred directly in aqueous solution to produce the* trans *bis-ligand complex without the formation of the intermediate tetrakis ligand complex. The* trans-*complexes are characterised by vibrational spectroscopy and elemental analysis.*

Introduction

In a previous study we found that complexes of the type PtL_4I_2 (L = pyridine, 3-picoline, 4-picoline, 4-ethylpyridine and 3,5-lutidine) can be thermally decomposed to give quantitatively, by loss of two pyridine ligands, the trans isomers PtL_2I_2 [1]. In the present work the utility of this route for the synthesis of *trans*-platinum bis-pyridine complexes has been extended to include other *trans*-bis-pyridine complexes with different coordinating anions. A recent report has shown that this synthetic route can be used to produce complexes of the type *trans*-$Pt(NMIz)_2X_2$ (X = Cl, Br, I; NMIz = N-methylimidazole) [2].

TABLE I. Analytical and Preparative Data.

Compounds (*trans* isomers)[g]	%C		%H		%N		Method of Preparation
	Found	Calc.	Found	Calc.	Found	Calc.	
$Pt(pyr)_2Cl_2$	28.4	28.3	2.39	2.36	6.67	6.60	a, b
$Pt(pyr)_2Br_2$	23.4	23.4	1.99	1.95	5.63	5.46	a, b
$Pt(pyr)_2(NCS)_2$	30.7	30.6	2.31	2.12	12.0	11.9	a, d
$Pt(2\text{-pic})_2Cl_2$	31.8	31.9	3.08	3.10	6.29	6.20	a, c
$Pt(2\text{-pic})_2Br_2$	26.6	26.6	2.76	2.59	5.21	5.18	a, c
$Pt(2\text{-pic})_2(NCS)_2$	33.8	33.8	3.11	2.81	11.4	11.3	a, d
$Pt(3\text{-pic})_2Cl_2$	31.8	31.9	3.07	3.10	6.06	6.20	e
$Pt(3\text{-pic})_2Br_2$	26.7	26.6	2.57	2.59	5.15	5.18	e
$Pt(3\text{-pic})_2(NCS)_2$	34.0	33.8	2.89	2.81	11.2	11.3	a, d
$Pt(4\text{-pic})_2Cl_2$	31.9	31.9	3.07	3.10	6.29	6.20	e
$Pt(4\text{-pic})_2Br_2$	26.7	26.6	2.59	2.59	5.26	5.18	e
$Pt(4\text{-pic})_2(NCS)_2$	34.0	33.8	3.10	2.81	11.2	11.3	f
$Pt(3,5\text{-lut})_2Cl_2$	35.1	35.0	3.69	3.75	5.78	5.84	e
$Pt(3,5\text{-lut})_2Br_2$	29.7	29.5	3.33	3.16	4.94	4.92	e
$Pt(3,5\text{-lut})_2(NCS)_2$	36.3	36.6	3.33	3.43	10.6	10.7	f

[a]Trans-bis-ligand product precipitated on addition of tetrakis ligand chloride solution to a concentrated aqueous solution of the appropriate anion. [b]Yellow solid obtained after heating the aqueous solution at 90 °C for 24 hours (Cl) and 12 hours (Br). [c]Yellow oil obtained after heating the aqueous solution at 90 °C for 2 hours. [d]Yellow crystals obtained a few minutes after mixing. [e]Product obtained by heating tetrakis ligand salt at 140 °C under vacuum for 8–12 hours. [f]Product obtained by heating tetrakis ligand salt at 100–120 °C under vacuum for 4 hours. [g]Yields in most cases are almost quantitative.

Experimental

Starting Materials

Commercially available pyridines (Aldrich) were used without further purification. Potassium tetrachloroplatinate(II) was synthesized via the hexachloroplatinate(IV) by the standard procedure [3].

Syntheses

trans-*Pt(4-picoline)$_2$(NCS)$_2$*

K_2PtCl_4 (1.0 g, 2.4 mmol) was dissolved in water (100 cm^3) and 4-picoline (6.0 cm^3, excess) added. The mixture was refluxed until a clear solution was obtained which was filtered rapidly into a cold saturated aqueous solution of sodium thiocyanate (excess). The tetrakis ligand complex [Pt(4-picoline)$_4$](NCS)$_2$ was obtained as a white crystalline solid in almost quantitative yield. The product was filtered, washed with ice cold water and dried in a vacuum desiccator over $CaCl_2$.

On heating the white solid at 100–120 °C *in vacuo* (0.1 mm Hg) for 4 hours a yellow solid was obtained which was crystallized from chloroform to give yellow crystals of *trans*-Pt(4-picoline)$_2$(NCS)$_2$. Other complexes were prepared similarly (see Table I).

trans-*Pt(3-picoline)$_2$(NCS)$_2$*

K_2PtCl_4 (1.0 g, 2.4 mmol) was dissolved in water (80 cm^3) and 3-picoline (4.0 cm^3, excess) added. The mixture was refluxed until clear and filtered rapidly into aqueous thiocyanate as described above. A pale yellow solution formed, from which on standing, yellow crystals were obtained. The product *trans*-Pt(3-picoline)$_2$(NCS)$_2$ was filtered, washed with water, dried in a vacuum desiccator over $CaCl_2$ and recrystallized from chloroform. Other complexes were prepared similarly (see Table I).

Physical Measurements

C, H, N analyses were performed by Beller Microanalytical Laboratory, Göttingen, Infrared spectra were obtained as KBr discs and Nujol mulls using Perkin Elmer models 457 and 283.

Results and Discussion

Examples of solid tetrakis ligand platinum(II) complexes containing the ion $[Pt(L)_4]^{2+}$ (L = pyridine, 2-, 3-, 4-picoline) are well documented [1, 4–7]. These have been isolated as salts of the type $[Pt(L)_4]X_2$ (X = coordinating or non-coordinating anion) and as Magnus type salts $[Pt(L)_4][PtX_4]$. They have been of interest as synthetic intermediates in the production of certain *trans*-isomers [1, 6–8] and also in redox studies of platinum systems [4, 9]. Their stability, however, appears to depend upon steric factors associated with the ligand and the nucleophilic characteristics of the anionic group.

The use of thermal decomposition of tetrakis ligand complexes $[M(L)_4]X_2$ as a means of producing *trans*-complexes of the type ML_2X_2 (M = Pt, Pd; L = NH_3. X= halogen) is well known and temperatures as high as 250 °C have been used [10–12]. This type of reaction probably results from an initial study by Reiset [10] who converted $[Pt(NH_3)_4]Cl_2 \cdot H_2O$ into *trans*-$Pt(NH_3)_2Cl_2$ by heating at 250 °C. Analogous thermal dissociations have been observed for palladium ammine systems using TGA and DTA analysis [12].

DTA and TGA studies on the complexes $[Pt(L)_4]I_2$ (L = pyridine, 3-picoline, 4-picoline, 4-ethylpyridine and 3,5-lutidine) indicate the endothermic loss of two pyridine ligands at 166 °C or less by a probable two step process to form the complexes *trans*-PtL_2I_2 [1]. This solid state nucleophilic displacement must involve the initial displacement of one pyridine by iodide to produce $[PtL_3I]I$, which then undergoes further reaction at the labilised site *trans* to the coordinated iodine to produce the *trans* isomer.

In the present study the general utility of this type of reaction has been explored in an attempt to provide a convenient route to *trans*-Pt(pyridine)$_2$X$_2$ complexes using readily available starting materials.

Aqueous solutions of the tetrakis-ligand platinum chloride complexes were prepared by refluxing an aqueous solution of K_2PtCl_4 with excess pyridine until a clear solution was obtained. The solutions were filtered hot into saturated aqueous solutions of sodium salts of the appropriate anion. In some cases white solids were obtained $[Pt(L)_4]X_2$ (L = 3-picoline; X = Cl, Br, L = 4-picoline; X = Cl, Br, NCS, L = 3,5-lutidine; X = Cl, Br, NCS), while the remaining tetrakis complexes were not isolated because of their high solubility in water and their tendency to dissociate to the *trans*-bis-ligand complexes in aqueous solution. When isolated and dried the solid tetrakis complexes always smell of the appropriate pyridine ligand, suggesting slow dissociation even at room temperature.

Thermal degradation of these compounds by heating under vacuum at temperatures of 100–150 °C for periods of 4–12 hours led to yellow solids, which were shown by elemental analysis (Table I) and infrared data (Table II) to be the bis-ligand complexes *trans*-PtL_2X_2. The infrared spectra of the tetrakis complexes $[Pt(L)_4]X_2$ did not show bands attributable to ν(Pt–X). However the yellow bis-ligand complexes exhibit strong singlet absorptions associated with Pt–X stretch (X = Cl, Br) and CN stretch (X = NCS), confirming the *trans* structures (Table II). Only one infrared active stretching mode should be observed for Pt–X in a *trans* planar structure. In the point group D_{2h} two stretching modes

TABLE II. Infrared Spectra (cm^{-1}).

Compounds (*trans* isomers)	νPt–X[a]	νCN(NCS)[b]
$Pt(pyr)_2Cl_2$	342[c]	
$Pt(pyr)_2Br_2$	248[c]	
$Pt(pyr)_2(NCS)_2$		2119
$Pt(2\text{-}pic)_2Cl_2$	339	
$Pt(2\text{-}pic)_2Br_2$	230	
$Pt(2\text{-}pic)_2(NCS)_2$		2119
$Pt(3\text{-}pic)_2Cl_2$	338	
$Pt(3\text{-}pic)_2Br_2$	260	
$Pt(3\text{-}pic)_2(NCS)_2$		2123
$Pt(4\text{-}pic)_2Cl_2$	348	
$Pt(4\text{-}pic)_2Br_2$	233	
$Pt(4\text{-}pic)_2(NCS)_2$		2120
$Pt(3,5\text{-}lut)_2Cl_2$	335	
$Pt(3,5\text{-}lut)_2Br_2$	259	
$Pt(3,5\text{-}lut)_2(NCS)_2$		2120

[a]Assignments made by comparison of spectra of analogous chloro, bromo and iodo complexes. [b]NCS coordinated as a thiocyanate via the sulphur atom. Ref. 13. [c]Previously reported Cl (343 cm^{-1}), Br (251 cm^{-1}). Refs. 14, 15.

involving the metal are to be expected: ν(M–X) (B_{3u}) and ν(M–L) (B_{2u}), both of which are infrared active. For the *cis* case both symmetric and antisymmetric stretching modes are expected for M–L and M–X ($A_1 + B_1$) [13].

The tetrakis-ligand complexes $[PtL_4]X_2$ (L = pyridine, 2-picoline; X = Cl, Br, NCS; L = 3-picoline, X = NCS) could not be isolated as solids from aqueous solution by treatment with a concentrated solution of the sodium or potassium salt of the appropriate anion. Instead the complexes *trans*-PtL_2X_2 were obtained directly, either as yellow crystalline solids or yellow oils. In the case of the thiocyanate derivatives yellow crystalline solids were obtained a few minutes after adding the hot solution of the tetrakis-ligand chloride to concentrated aqueous thiocyanate. This rapid reaction probably reflects the strong nucleophilic characteristics of the thiocyanate ion, coupled with a certain instability associated with the tetrakis cation itself. For steric reasons it is understandable why the reaction was rapid in the case of 2-picoline. The fact that solid tetrakis-ligand complexes were isolated for 4-picoline and 3,5-lutidine may be attributed to the increased basicity of these ligands (4-picoline $pK_b = 7.98$, 3,5-lutidine $pK_b = 7.85$). In the case of pyridine its weaker basicity ($pK_b = 8.75$) probably accounts for the lability of the system, while for 3-picoline perhaps steric factors exist as well. In the cases of the chloro- and bromo-derivatives the reactions were much slower (periods of up to 24 hours were required), reflecting the weaker nucleophilic characteristics of these ligands.

Conclusion

The broad utility of this method of producing *trans*-pyridine complexes PtL_2X_2 by the reaction of a readily available tetrakis complex $[Pt(L)_4]Cl_2$ with excess of an appropriately chosen coordinating anion has been well demonstrated and other work [2] suggests a more general applicability to include other ligand systems as well.

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