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Aminobenzonitrile Compounds of Platinum(II) and Palladium(II)

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The complexes [ML_2X_2] where M = Pt and Pd; L = 2,3 or 4-aminobenzonitrile and X = Cl and Br were synthesized. The cis-*compounds of platinum were prepared by the direct reaction of K_2PtX_4 and L. Using the same conditions, K_2PdX_4 produced* trans-*[PdL_2X_2]. The* trans-*compounds of platinum were obtained from the isomerization of the* cis-*isomers. The aminobenzonitrile ligands are monodentate and are bonded to the metal through their amino groups.*

Introduction

Aniline complexes of platinum, *cis*-[PtL_2Cl_2] (where L = aniline derivative) were reported to isomerize very easily in organic solvents, even without the presence of the free ligand as catalyst [1]. Our recent work [1–3] has shown that the isomerization factor of *cis*-[$Pt(am)_2Cl_2$], (am = amine) must be taken into consideration in order to accurately estimate the antitumor activity of platinum complexes. This factor is important, since *trans*-isomers have no antitumor properties.

We have now prepared platinum and palladium complexes with cyano substituted aniline, and have studied their isomerization reactions. Aromatic nitrile complexes of platinum and palladium have already been reported. Thus cyano-substituted anilines could act as bidentate or bridging ligands. An infrared study of the complexes [$M(C_6H_5CN)_2Cl_2$] has shown that the palladium compound is the *trans*-isomer, while the platinum compound is the *cis*-isomer [4]. In this work, we have studied platinum and palladium compounds with *ortho- meta-* and *para*-aminobenzonitrile.

Experimental

The preparations of the K_2PtBr_4, K_2PdCl_4 and K_2PdBr_4 solutions have been reported previously [2–3].

cis-[PtL_2X_2] *and* trans-[PdL_2X_2]

An aqueous solution (20 ml) containing one mmol of K_2PtX_4 or K_2PdX_4 was mixed with 5 ml of an alcohol solution containing 0.25 g of L (L = *o*-, *m*- or *p*-aminobenzonitrile) and stirred at room temperature for six to ten hours. The yellow precipitate was collected by filtration, washed with water, and air-dried. It was then washed with ether and dried under vacuum at room temperature. Yield: 65–80%.

Trans-[PtL_2Cl_2]

0.5 of *cis*-[PtL_2Cl_2] and 0.1 g of L were mixed in 30 ml of dimethylacetamide (DMA) and stirred for ten hours. The solution was then evaporated to dryness. The product was washed with ether and dried in vacuum at room temperature. Yield: 80%.

Trans-[PtL_2Br_2]

0.5 g of *cis*-[PtL_2Br_2] was dissolved in 3 to 5 ml of DMA and stirred at room temperature. Within 5 minutes a precipitate appeared. Thirty minutes later the precipitate was collected by filtration, washed with ether, and dried under vacuum at room temperature. Yield: 60%.

Results and Discussion

K_2MX_4 (M = Pd, Pt and X = Cl, Br) reacts with *o*-, *m*- and *p*-aminobenzonitrile (L) in a water–ethanol solution to give compounds which according to the results of the elemental analyses (Table I), show the experimental formula ML_2X_2.

The compounds are not ionic and their infrared spectra showed some M–X stretching bands. Since both platinum(II) and palladium(II) usually form four-coordinated compounds, this formula suggested that the aminobenzonitrile ligands were monodentate with either the amino ($-NH_2$) or the nitrile (–CN) group as the coordinating site. Nitrile ligands bind themselves to platinum in almost a straight line. A

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TABLE I. Elemental Analysis of the [M(ABN)$_2$X$_2$] Complexes.*

	%C	%H	%X
cis-[Pt(2ABN)$_2$Cl$_2$]	33.47	2.39	14.14
	33.57	2.47	13.94
cis-[(Pt(2ABN)$_2$Br$_2$]	28.42	2.03	27.07
	28.74	2.09	26.25
trans-[Pd(2ABN)$_2$Cl$_2$]	40.78	2.43	17.23
	40.49	2.83	17.30
trans-[Pd(2ABN)Br$_2$]	33.40	2.00	31.81
	33.40	2.43	32.78
cis-[Pt(3ABN)$_2$Cl$_2$]	33.47	2.39	14.14
	33.25	2.53	14.05
cis-[Pt(3ABN)$_2$Br$_2$]	28.42	2.03	27.07
	29.09	2.16	26.59
trans-[Pt(3ABN)$_2$Br$_2$]	28.42	2.03	27.07
	29.20	2.55	26.20
cis-[Pt(4ABN)$_2$Cl$_2$]	33.47	2.39	14.14
	33.59	2.48	14.37
cis-[Pt(4ABN)$_2$Br$_2$]	28.42	2.03	27.07
	28.04	2.25	26.25
trans-[Pt(4ABN)$_2$Br$_2$]	28.42	2.03	27.07
	29.30	2.55	26.10

*Calculated values in first row.

structure determination of *cis*-[Pt(CH$_3$CN)$_2$Cl$_2$) has shown that the segment Pt–N≡C–C is almost linear [5]. Because of this observation, molecular models have shown that 2-aminobenzonitrile cannot form a six-membered chelate, but all three isomers could form bridges between two different platinum atoms. However, attempts to prepare complexes containing these ligands as bidentates failed, even when an excess of K$_2$MX$_4$ (M:L = 2:1) was used.

The infrared spectra of the compounds [ML$_2$X$_2$] were measured in order to determine whether the amino or the nitrile group was the binding site. Upon coordination of the ligands, the NH stretching frequency is shifted to a lower region by about 150 cm^{-1} while the CN is also shifted by about 10 cm^{-1}. Since the NH stretching is more affected than the –CN frequency, we can reason that the –NH$_2$ group is the coordinating site. The smaller shift observed for the –CN vibration could be due to the effect of the coordination of the –NH$_2$ group through the aromatic ring.

Furthermore, the properties and the chemical reactions of these [ML$_2$X$_2$] complexes suggest that they are amine compounds rather than nitrile compounds. For example, K[Pt(DMSO)Cl$_3$] and aniline or amine (am) in water immediately give a precipitate identified as *trans*-[Pt(DMSO)amCl$_2$], while benzonitrile does not react with K[Pt(DMSO)Cl$_3$]. Aminobenzonitrile (ABN), like aniline, reacts rapidly with K[Pt(DMSO)Cl$_3$] to give *trans*-[Pt(DMSO)(ABN)Cl$_2$], suggesting that the coordinating site is the amino group. Furthermore the compounds *cis*-[PtL$_2$X$_2$] isomerize to the *trans*-isomers when dissolved in DMA. This behavior is similar to that of *cis*-[Pt(aniline)$_2$X$_2$] [1].

K$_2$PtX$_4$ reacts with L in a water–ethanol solution to give *cis*-[PtL$_2$X$_2$]. The *trans*-isomers can be prepared from the isomerization of the *cis*-isomers in DMA. K$_2$PdX$_4$ reacts under the same conditions with the nitrogen bases (L) to give the *trans*-isomers [6]. A few *cis*-isomers of palladium(II) have been prepared [3], but usually they are unstable and change easily to the *trans*-isomers.

The compounds [PdL$_2$X$_2$] after refluxing with free L were found unchanged, indicating that the palladium compounds have the *trans*-configuration.

The assignment of the M–Cl stretching band in the far infrared region must be done carefully since the free ligand has a broad and weak band at 340 cm^{-1}. Upon coordination to the metal, this band becomes narrow and increases in intensity. For example *trans*-[Pd(2ABN)$_2$Cl$_2$] (ABN = aminobenzonitrile) has two bands at 331 cm^{-1} (vs) and at 358 cm^{-1} (m) while *trans*-[Pd(2ABN)$_2$Br$_2$] has only one band at 350 cm^{-1} (m). The band at 331 cm^{-1} was therefore assigned to the Pd–Cl stretching vibration. The spectra of *trans*-[Pd(3ABN)$_2$X$_2$] and *trans*-[Pd(4ABN)$_2$X$_2$] are similar to the spectrum of the 2ABN compound.

The *cis*-compounds of platinum have bands at 359(s) and 329(vs) cm^{-1} (L = 2ABN), at 344(sh) and 330(vs) cm^{-1} (L = 4ABN) and at 328 (vs,br) cm^{-1} (L = 3ABN). The band at higher frequency is sensitive to the ligand configuration. It could therefore be a mixture of Pt–Cl stretching and some deformation mode of the ligands. The band in the lower region becomes narrower and more intense in the *trans*-complexes.

When the compounds are allowed to stand for a long time in DMF or when heated slightly, they gradually become blue. This behavior is similar to some other nitrile compounds [7], but in these cases the nitrile ligands were bonded to platinum.

Howe-Grant *et al.* [8] reported that platinum compounds containing aromatic non-leaving ligands could intercalate as well as bind covalently to DNA and *o*-phenylenediamine compounds of platinum have been reported to have antitumor activity [9, 10]. The aminobenzonitrile compounds of platinum may also display these properties.

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