Complex salts of platinum with ethylenediamine and propanediamine [PtCl(diamine)L][PtCl$_3$L]

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Abstract

Reaction of anionic platinum salts K[PtCl$_3$L], where L = NH$_3$, DMSO or ethylene (C$_2$H$_4$) with the diamines ethylenediamine or 1,3-propanediamine in 2:1 stoichiometry gives as products the complex salts [PtCl$_3$L][PtCl(diamine)L]. No evidence of complexes containing two platinum atoms linked by these short-chain diamines was found. The complex salts were characterised by ^{1}H and ^{195}Pt NMR spectroscopy.

Introduction

The reaction of diamines H$_2$N(CH$_2$)$_n$NH$_2$ with an anion such as K[PtCl$_3$(NH$_3$)] in a 1:2 stoichiometry gives bis(platinum) complexes of general formula [{*cis*-PtCl$_2$(NH$_3$)}$_2$H$_2$N(CH$_2$)$_n$NH$_2$] [1, 2]. These complexes are of interest for their chemical and biological properties [3, 4]. The synthetic approach employed is only useful for diamines of chain length $(n) > 4$ because for $n = 2$ and 3 chelation of the diamine to the same Pt atom occurs in preference to bridge formation. During our studies on these systems we noted a report [5] on the existence of a bridging ethylenediamine formed by reaction with Zeise's salt K[PtCl$_3$(C$_2$H$_4$)]. This note reports on the identification of the products from the 1:2 reaction of H$_2$N(CH$_2$)$_n$NH$_2$, $n = 2$ or 3, with the salts K[PtCl$_3$L], L = NH$_3$, DMSO or C$_2$H$_4$, as complex salts of general formula [PtCl(diam)(L)][PtCl$_3$L].

Experimental

Starting materials and physical methods

The complexes K[PtCl$_3$(NH$_3$)] and K[PtCl$_3$(DMSO)] were prepared by the literature methods [6, 7] respectively. Zeise's salt was purchased from Aldrich. IR spectra were obtained as KBr discs on Nicolet FT6000 series and Perkin-Elmer 1430 spectrophotometers. NMR spectra were run on Bruker 250 and 270 MHz spectrometers. ^{195}Pt NMR spectra (250 MHz) were run in DMA with d$_6$-acetone as external lock with reference to a Na$_2$PtCl$_6$ solution in D$_2$O. Samples were run at a pulse width of 15 μs and usually a sweep width of 30 KHz was used and 5000–10 000 scans were adequate. All shifts are positive to lower shielding. Elemental analyses were by Robertson Laboratories, Madison, NJ.

Preparation of complexes

To prepare the salts of the title a general method is to add a solution of the appropriate diamine in MeOH to a two-fold stoichiometric excess of salt K[PtCl$_3$L] in either MeOH (L = NH$_3$ or DMSO) or H$_2$O (L = C$_2$H$_4$). Upon stirring overnight the products precipitate out and may be filtered, washed with water and acetone and dried. The properties are given in Table 1. Salts of type [Pt(diam)(L)Cl]Cl are obtained by use of excess of diamine in which case no intermediate products are observed or could be isolated.

Results and discussion

The reaction of one equivalent of propanediamine (prop) with two equivalents of the anions [PtCl$_3$L]$^-$ (L = NH$_3$, DMSO) presumably proceeds through initial formation of the [PtCl(prop)L] followed by precipitation of the least soluble ion pair [PtCl(diam)(L)][PtCl$_3$L]. Typical characterisation data are given in Table 1. The crystal structure resolution of the ethylenediamine derivative [PtCl(en)(DMSO)][PtCl$_3$(DMSO)] has definitively

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TABLE 1. Analytical and NMR data for [PtCl(diam)L][PtCl$_3$L][a]

Complex	L	diam	Anal.: found (calc.) (%)			δ(^{1}H NMR) [PtCl(diam)L]	[PtCl$_3$L]	δ(^{195}Pt)
			C	H	N			
I	NH$_3$	prop	5.6(5.6)	2.4(2.5)	8.7(8.8)	1.89(m), 2.75(45)		−1750, 2460
II	Me$_2$SO	prop	10.9(11.1)	3.0(2.9)	3.2(3.7)	1.90(m), 2.80(45) 3.51	3.55	−2955, −3260
III	C$_2$H$_4$	en	11.0(11.1)	2.3(2.5)	4.3(4.3)	2.91(40) 4.72(56)	4.21(65)	−2712, −3168

[a] All spectra in d$_7$-DMF. Values in parentheses are (Pt–H) coupling constants in Hz when clearly observed. ^{1}H NMR chemical shifts relative to TMS, ^{195}Pt NMR chemical shifts relative to PtCl$_6^{2-}$. All complexes give broad bands at 6–8 ppm assigned to NH$_2$ protons.

confirmed the mixed salt nature of the products [8]. With excess of diamine the known [PtCl(diam)L]Cl is formed as expected [9, 10].

In view of these results we reexamined the early report of a bis(platinum) complex with bridging diamine as the product of reaction of Zeise's salt with ethylenediamine. The accumulated evidence however rules out the presence of bridging ethylenediamine as previously postulated [5]. The 2:1 product, complex **III**, shows two peaks at −2712 and −3168 ppm in the ^{195}Pt NMR spectrum (Fig. 1) confirming the mixed salt nature of the compound. Zeise's salt itself gives a peak at −2705 ppm in d$_7$-DMF, in agreement with published values [11]. The ^{1}H NMR spectrum of complex III, Fig. 1, also displays two distinct triplets, arising from Pt–H coupling, for the two independent ethylene units at 4.21 (*J*(Pt–H) = 64 Hz) and 4.72 (*J*(Pt–H) = 56 Hz) ppm. By analogy with the chemical shifts and coupling constants in mixed amino acid/olefin platinum(II) complexes [PtCl(olefin)(*N*,*O*-amino acid)] [12] we assign the upfield shift to that of the [PtCl$_3$(C$_2$H$_4$)]$^-$ anion. The olefin protons in the [PtCl(en)C$_2$H$_4$)]$^+$ cation are broadened with respect to those of the Zeise's anion probably due to differences in restricted rotation around the platinum–olefin bond [13]. In DMF, broad signals assigned as the NH$_2$ protons appear at 6–8 ppm. Further evidence for the mixed salt nature of complex III may in fact also be obtained from analysis of the IR spectrum where two distinct bands at 396 and 402 cm^{-1} are seen. In Zeise's salt itself there is only one band in this region at 407 cm^{-1} attributed to ν(Pt–C$_2$H$_4$) [14].

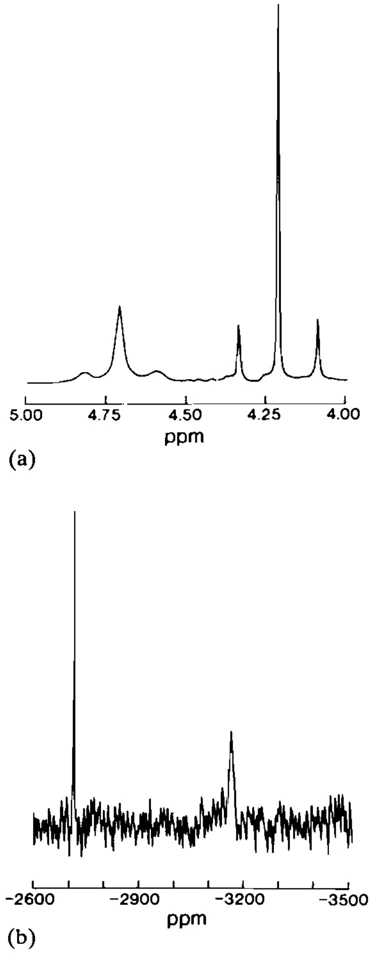
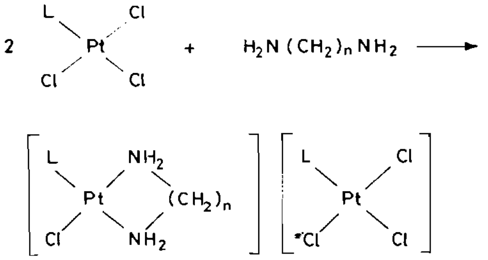


Fig. 1. ^{1}H (a) and ^{195}Pt (b) NMR spectra of [PtCl(en)(C$_2$H$_4$)][PtCl$_3$(C$_2$H$_4$)]. For the ^{1}H NMR spectrum only the olefin region is shown.

In 1:1 stoichiometry a pale yellow solution with only one ^{195}Pt NMR signal at −3170 ppm indicative of the [PtCl(diamine)(olefin)] coordination sphere is obtained. The reaction thus represents a simple preparative route to these cations; few examples of which have in fact been reported [15, 16]. The complexes are of interest because of the demonstrated reactivity of the olefin in the closely related

$[PtCl_2(C_2H_4)L]$ (L = for example with *N,N,N′,N′*-tetramethylethylenediamine, Me_4en) [17, 18]. In this respect, attack on the olefin is probably facilitated by the presence of bulky substituents on the amine nitrogens, which may slow down the chelate formation we have observed.

In summary, the reactions of ethylene- and propanediamine with $[PtCl_3L]^-$ in 1:2 stoichiometry give the mixed salts [PtCl(diamine)L][$PtCl_3L$] and complexes containing bridging diamine are not obtainable by this route (*n* = 2,3 L = Me_2SO, NH_3, C_2H_4).



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