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A Platinum(IV) Complex Containing a Cationic Amine Ligand

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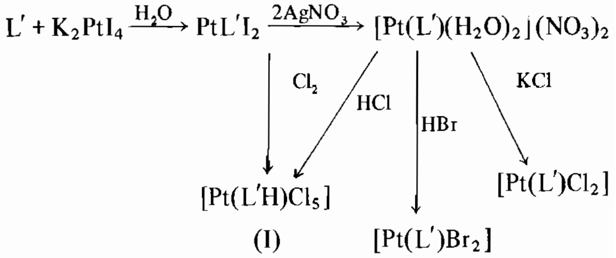


During the last five years there has been increasing interest in complexes containing metals coordinated to cationic ligands, such ligands containing donor atoms N, P, As, O.[1] We do not know of any such complexes of platinum, and none containing a metal in a high oxidation state. Here we wish to report the formation of a cationic ligand formed during the oxidation of a platinum(II) complex.

We are currently involved in the preparation of a series of platinum(II) complexes of N-substituted ethylenediamines and the subsequent reaction of $[Pt(N,N)(H_2O)_2]^{2+}$ species with concentrated hydrochloric acid or chlorine gas to give platinum (IV) derivatives. We have discovered one sterically controlled borderline in the preparation of these complexes. Thus, N-isopropylethylenediamine forms a stable $[Pt(L)Cl_2]$ complex which can be oxidised to $[Pt(L)Cl_4]$, but the more sterically crowded N,N,N′-triisopropylethylenediamine (L″) does not appear to form any complex with platinum (IV). N,N-diisopropylethylenediamine (L′) presents us with a borderline case of complexing ability:

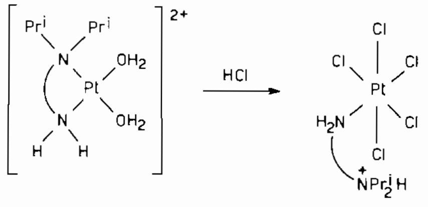
$H_2NCH_2CH_2NHPr^i$ (L) $H_2NCH_2CH_2NPr^i_2$ (L′)

$Pr^iHNCH_2CH_2NPr^i_2$ (L″)

This ligand reacts with K_2PtI_4 in aqueous solution to produce *cis*-$[Pt(L)I_2]$ in 92% yield; addition of two moles of $AgNO_3$ with stirring for ~ 18 hr followed by filtration yields *cis*-$[Pt(L)(H_2O)_2]^{2+}$ in solution (see Scheme). The presence of this ion is confirmed by reaction with excess aqueous KCl and warming to yield *cis*-$[Pt(L')Cl_2]$. However, addition of excess hydrochloric acid and heating to boiling until chlorine gas is evolved leads to the deposition of a yellow solid (I). *Analyses*: Found C, 18.6; H, 4.1; N, 5.7; Cl, 33.9%. $PtC_8H_{21}N_2Cl_5$ requires C, 18.6; H, 4.1; N, 5.4; Cl, 34.3%. A smaller yield of (I) may also be obtained by chlorine oxidation of $[Pt(L')(H_2O)_2]^{2+}$.

Complex (I) is a non-conductor in nitromethane. The infrared spectrum of free ligand L′ exhibits $\nu(NH_2)$ at 3356 (m) and 3280 (m) cm^{-1} and in complex (I) the presence of $\nu(NH_2)$ at 3252 (m), 3220 (m) and 3168 (m) indicates that the primary amine group is unquaternised and is coordinated.[2] Complex (I) also exhibits a broad band at 2420 cm^{-1} assignable to $\nu(\overset{+}{N}H)$ of the protonated L′H.

We thus suggest that the presence of two isopropyl groups on a nitrogen weakens the Pt–N bond and makes it susceptible to protonation:



(I)

It is interesting to observe, however, that reaction of $[Pt(L)(H_2O)_2]^{2+}$ with HBr leads neither to oxidation nor protonation, but to *cis*-$[Pt(L)Br_2]$. Moreover, we have independently synthesised L′HCl and find that this species has no complexing ability towards platinum. It is thus likely that after protonation the platinum(IV)–amine bond is stabilised by some lattice energy effect.

Acknowledgements

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