Diaminehalogenoplatinum(II) complex reactions with DMSO

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DMSO (dimethylsulphoxide) as a solvent has been used in studies of biological effects of several cis-bis(amine)dihalogenoplatinum(II) complexes[1] in cases where the solubility in water was too low. In the case of [Pt(n-n)X_2] (X=Cl, Br, and I; (n-n)=1,2-ethanediamine (en) and 1,3-propanediamine (tn)) in DMSO solution, the solvent reacts by substituting one halogenide by DMSO over time. The substitution reactions were followed using changing integrals of signals in NMR-spectroscopy. The rate constant for [PtenCl_2] was found to $1.1*10^{-4}$ s^{-1} at 300 K and from kinetic runs at different temperatures the energy of activation was estimated as 80 $kJ*mol^{-1}$.
The rate constant depends on the size of halogenide and was found to increase by a factor of 40 for [PtenI_2] relative to its chloro- analogue. In the tn-series rates were a little faster than in the en-series. The relative rates when varying the halogenide as leaving group was opposite to that found[2] for the substitution of halogenide by pyridine in $[PtdienX]^+$ in aqueous solution.

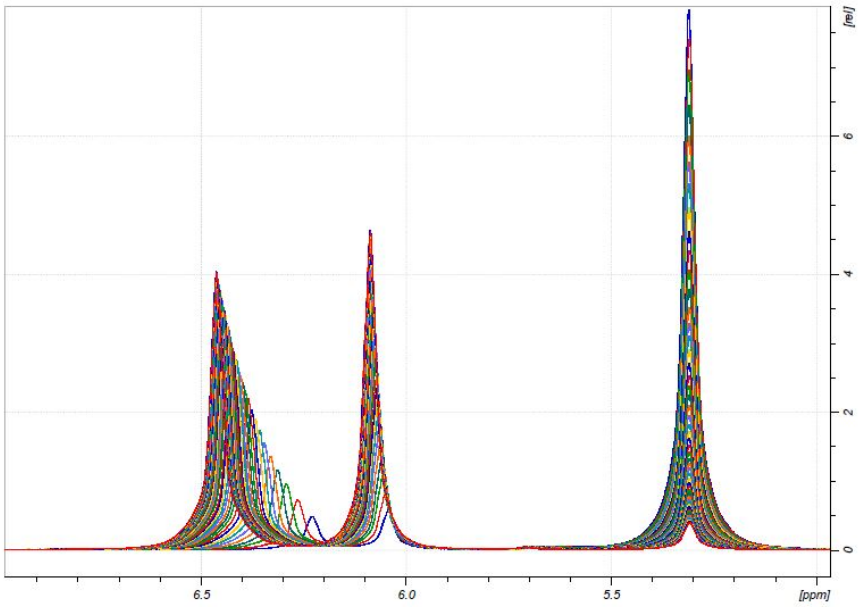

Figure 1: Amine-proton signals in ^{1}H-NMR spectra (Bruker AC 250 at 300K) (Δt=10 min.) during solvolysis of PtenCl_2 in DMSO (C_{Pt}=.15M). Disappearing signals to the right (staying at 5.3 ppm); appearing signals to the left. The positions of the last two signals extrapolated back to t=0 coincides with those observed for [PtenCl(DMSO)]ClO_4

The products [Pt(n-n)DMSOX]X were easily isolated, and the DMSO exchange (in DMSO) was found to be slightly slower than the solvolysis reactions in the en-series, again with iodide giving rise to the most labile system.
It is easily observed in Fig. 1, that the positions of the emerging signals (of the non-equivalent amine protons in the product) change. This change was taken as evidence of ion pair formation in DMSO solution of $[Pt(n-n)DMSOX]^+,X^-$ in fast equilibrium with the solvated ions. Among the six [Pt(n-n)DMSOX]X studied here, ion pair formation was found to be modest to almost negligible with a formation constant of 30 M^{-1} in the case of [PtenDMSOCl]Cl as the largest.

1. J.M. Pascoe and J.J. Roberts, Biochem. Pharmacol., 23 (1974) 1345
2. F. Basolo, H.B. Gray, and R.G. Pearson, J.Amer.Chem.Soc., 82 (1960) 4200-4203