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Preliminary communication

The X-ray Structure of a Five-coordinate Platinum(II) Complex Cation

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SUMMARY

X-ray structure analysis of the stable cationic complex (2,2'-bipyridyl)-chloro(o-isopropenyl-N,N-dimethylaniline)platinum(II) confirms that it is formally five-coordinate, but if 3c-4e bonding of the bipyridyl ligand and Pt(II) is invoked the complex may be regarded as obeying the 16 electron rule which dominates platinum(II) chemistry.

Reaction of dichloro(o-isopropenyl-N,N-dimethylaniline)platinum(II), ($PtCl_2IMN$), with 2,2'-bipyridine (bipy) and sodium perchlorate in chloroform/acetone (1.1) solution gives a compound which analyses for $[Pt(bipy)Cl(IMN)][ClO_4]$ (I). N.m.r. evidence shows that in solution Pt(II) atom in (I) is formally five-coordinate, the conductivity in nitrobenzene shows that the complex is singly charged, and that the structure of the cation presists in the solid state is indicated by the i.r. spectrum.[1] This is the first five-coordinate platinum(II) complex cation to be isolated and preliminary results of its X-ray structure analysis are reported here.

Crystals of $[C_{21}ClH_{23}N_3Pt]$ $[ClO_4]$ (I) are monoclinic, spacegroup $P2_1/c$, a = 16.715, b = 10.278, c = 13.990 Å, β = 107.24°, V = 2295.5 Å^3, D_c= 1.87 g cm^{-3} for Z = 4. The crystals diffracted rather weakly so that solution and refinement of the structure was based on only 691 unique reflections, $I/\sigma(I)>2.0$. The phenyl ring was treated as a rigid group (C–C 1.395 Å) and full matrix refinement of the group and atomic parameters (Pt anisotropic) has given an R-factor of 0.068.

and N(3), thus allowing the Pt orbital to overlap sp^2 orbitals from both bipyridyl nitrogens as shown in Fig.2 By invoking three-centre four-electron bonding of the platinum and the bipyridyl nitrogen atoms it is possible to rationalise the structure of the formally five-coordinate cation in terms of the preferred square planar coordination of platinum(II). Furthermore in 3c-4e bonding of this type, one electron pair would be accommodated in an essentially non-bonding molecular orbital (which would have predominately ligand character)[2] and thus the 16-electron rule, which dominates platinum(II) chemistry, would be obeyed. The stability of other formally five-coordinate platinum(II) complexes, shown by X-ray analysis to have very distorted trigonal-bipyramidal coordination geometries with small equatorial N-Pt-N angles,[3,4] could also be related to this type of 3c-4e bonding.

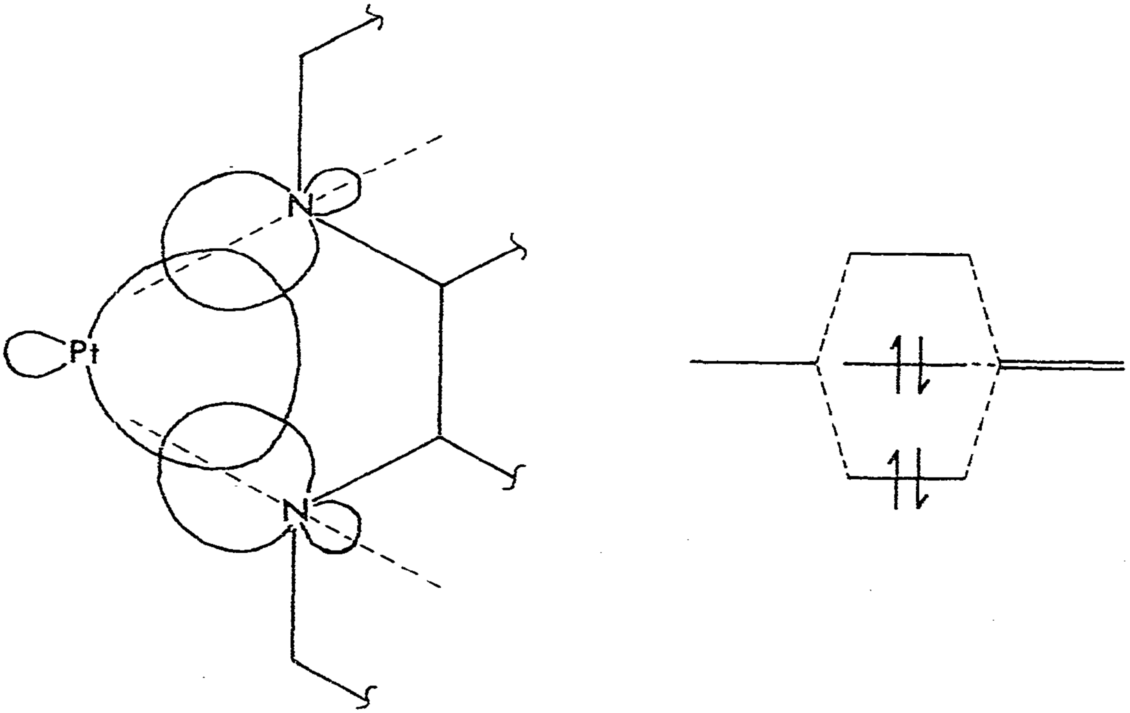

Fig. 2. A schematic representation of orbital overlaps in the Pt(II) bipyridine bonding and the corresponding energy level diagram.