The Influence of Non-co-ordinated Counter-ions on the Bonding Modes of Ambidentate Ligands

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THE bonding modes of various ambidentate ligands have been shown to be subject to several directive influences, among them the nature of the co-ordinated metal atom (for the ligands NO_2^-,[1] NCS^-,[2] CN^-,[3] $SeCN^-$,[4] urea,[5] methylthiourea,[6] dimethyl sulphoxide,[7] tetrahydrothiophen oxide[8]); the electronic character of other ligands in the co-ordination sphere (NCS^-)[9]; the steric character of other ligands in the co-ordination sphere (NO_2^-,[10] NCS^-,[11] $NCSe^-$ [12]); the physical state of the complex (NO_2^-,[13] NCS^- [14,15]); and the mechanism of the reaction used to synthesize the complex (NO_2^-,[1] NCS^-,[16] CN^- [17]). We now report the first observation of the influence of the nature of a *non-co-ordinated* group on the bonding mode of an ambidentate ligand.

$[Pd(Et_4dien)SeCN](BPh_4)$ (Et_4dien = 1,1,7,7-tetraethyldiethylenetriamine) has been shown[12] to undergo an *Se*- → *N*-bonded isomerization in a variety of solvents. Surprisingly, once isolated in the solid state, the *N*-bonded isomer reisomerizes to the *Se*-bonded form, as shown by the disappearance of the C–N and C–Se stretching bands at, respectively, 2085 and 618 cm.$^{-1}$, and the reappearance of the corresponding bands at 2121 and 533 cm.$^{-1}$. Evidently, in forming the crystal, the steric interaction of the selenium atoms with the non-co-ordinated tetraphenylborate ions is more important than their interaction with the ethyl groups of the co-ordinated amine. This suggested that the analogous $[Pd(Et_4dien)NCS](BPh_4)$ complex might behave in a similar manner, whereas, if a relatively small counter-ion were employed, no *N*- → *S*-bonded solid-state isomerization would be expected to take place.

An example of the latter case has already been reported: $[Pd(Et_4dien)SCN][NCS]$ undergoes the "normal" *S*- → *N*-bonded isomerization in solution and in the solid state.[18] $[Pd(Et_4dien)SCN][BPh_4]$ was accordingly prepared, isomerized to the *N*-bonded form in solution, and isolated, by a procedure analogous to that employed[12] in the synthesis of the selenocyanate isomers. (Both syntheses are best carried out with NaXCN in place of KXCN, in order to avoid contamination of the product by $KBPh_4$.) As shown by the change in frequency of the C–N stretching band from 2088 to 2113 cm.$^{-1}$, the predicted *N*- → *S*-bonded solid-state isomerization does indeed take place, albeit at a lower rate than that of the selenocyanate complex, owing, presumably, to the smaller size of the sulphur atom.

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