Solvent Control of the Bonding Mode of Co-ordinated Thiocyanate Ion

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Summary The bonding mode of co-ordinated thiocyanate ion in solution has been observed to be dependent upon the nature of the solvent, Pd–SCN bonding being promoted by solvents having high dielectric constants, and a mixture of Pd–NCS, Pd–SCN, and Pd–SCN–Pd bonding being formed in solvents having low dielectric constants.

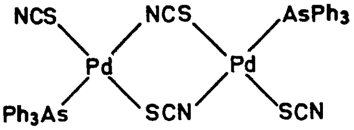
THE bonding modes of various ambidentate ligands have been shown to be subject to a variety of directive influences.[1,2] The occurrence of a specific solvent effect has been noted in only a few cases (one involving the co-ordinated nitrite ion[3] and three rather disparate, largely unexplained examples involving the thiocyanate ion[2,4,5]). In an effort to ascertain the nature of the role played by the solvent in linkage isomeric systems, we have systematically studied the effects of dissolution of the linkage isomers $[Pd(AsPh_3)_2(SCN)_2]$ and $[Pd(AsPh_3)_2(NCS)_2]$ in a series of solvents of differing polarity. It has been shown[6] that the *N*-bonded isomer is the more stable complex in the solid state. The isomers are most easily distinguished by their characteristic ν_{CN} bands[6] (*S*-bonded, 2119 cm^{-1}, s, sp; *N*-bonded, 2089 cm^{-1}, s, br; both measured as Nujol mulls).

Two distinctly different types of behaviour were observed in this study. Solutions of *either* isomer (*ca.* 10^{-2}M) in $Me_2N{\cdot}CHO$ or Me_2SO exhibited identical i.r. spectra (ν_{CN} 2115 and 2058 cm^{-1}) which did not change with time. The 2115 cm^{-1} band is assigned to the *S*-bonded isomer, and the 2058 cm^{-1} band is characteristic of ionic thiocyanate in these solvents. The addition of KNCS to the solutions resulted in an enhancement of the intensity of both peaks, whereas refluxing the $Me_2N{\cdot}CHO$ solutions resulted in an increase in intensity of the ionic peak at the expense of the *S*-bonded peak. Solutions of either isomer in C_5H_5N, Me_2CO, MeCN, PhCN, or adiponitrile exhibited only a single sharp ν_{CN} peak in the range 2120—2113 cm^{-1}. No evidence for the presence of any *N*-bonded species was observed in any of the solutions using these seven solvents (Group A).

Dissolution of the isomers in C_6H_6, CCl_4, $CHCl_3$, CH_2Cl_2, cyclopentanone, cyclohexanone, or $PhNO_2$ (Group B) produced dramatically different results. The i.r. spectra, which again were found to be independent of the isomer dissolved and invariant with time, exhibited three ν_{CN} bands in the following ranges: 2170—2153br, 2125—2118sp, and 2095—2083br cm^{-1}. The highest frequency band, which is characteristic[7] of bridging thiocyanate groups, *e.g.* Pd–SCN–Pd, is the most intense of the three. The intensities of the middle frequency band, assigned to *S*-bonded thiocyanates, and the lowest frequency band, assigned to *N*-bonded thiocyanates, are generally comparable. However, since the molar extinction coefficients of the ν_{CN} bands of *S*-bonded thiocyanates have been found[8] to be 2—8 times smaller than those of the ν_{CN} bands of *N*-bonded thiocyanates, it is clear that, initially, the number of *N*-bonded thiocyanates present in the solutions is the smallest of the three bond types represented. When Ph_3As was added stepwise to the solutions, the bridging peak was observed to diminish in intensity, concurrent with the marked growth of the *N*-bonded peak. It was not possible to determine from the spectra whether or not the number of *S*-bonded thiocyanates changes in the process because of the large degree of overlap between the *S*-bonded peak and the growing, much more intense, broad *N*-bonded peak. However, the data clearly indicate that, under conditions where bridging is minimized, the *N*-bonded mode is a major component in all of the Group B solutions.

The data can be rationalized in terms of equilibria involving *trans* *N*- and *S*-bonded mononuclear thiocyanate complexes (including, perhaps, a mixed bonding-mode mononuclear complex), free Ph_3As, and dinuclear bridged complexes of the type shown in the diagram.

The formation and cleavage of the latter provides an easy pathway for the interconversion of the linkage isomers. Although other isomeric dinuclear species are undoubtedly involved in the equilibria, the one shown is the predominant form present prior to the addition of Ph_3As insofar as the bonding mode of its terminal thiocyanates is concerned for, as previously mentioned, *N*-bonding is minimized when bridging is maximized. This would also be anticipated in view of the fact that only one π-electron-withdrawing Ph_3As is co-ordinated to each palladium(II).[6] Jennings and Wojcicki[9] have also noted the tendency of complexes of the type $[Rh(AsR_3)_2(CO)NCS]$ to form dinuclear thiocyanate-bridged species in solution.



The Group A solvents may be differentiated from those in Group B in that the former generally exhibit larger dipole moments, dielectric constants, and internal pressures. There are exceptions in each case, the most glaring being pyridine in Group A and nitrobenzene in Group B. However, pyridine is a good co-ordinating solvent, despite its relatively low polarity and dielectric constant, and nitrobenzene is a poor co-ordinating solvent, its relatively high dipole moment and dielectric constant notwithstanding, indicating the importance of specific interactions which are not reflected in the physical parameters chosen.

Nonetheless, the recent treatise by Klopman,[10] concerning chemical reactivity and the concept of charge- and frontier-controlled reactions, appears relevant. One of the predictions resulting from Klopman's equations is that solvents with high dielectric constants tend to enhance frontier orbital-controlled interactions whereas those with low dielectric constants favour charge-controlled reactions. In the present case, this implies that the former solvent type (Group A) should promote Pd–SCN bonding, whereas the latter (Group B) should promote Pd–NCS bonding—precisely the general bonding pattern observed. It should be noted that the solvent-induced isomerization of $[Co(CN)_5SCN]^{3-}$ observed by Gutterman and Gray[2] is also in the same direction. Indeed, these examples represent the first experimental verification of this prediction. That there are a few exceptions to the general trend is to be anticipated, for as Klopman points out,[10] other factors like those associated with the Coulomb interaction are varying at the same time.

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