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

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Summary Co^{III}–SCN bonds can be formed in the presence of suitable ligands but, for some ligands, isomerisation occurs in solution to give a mixture of linkage isomers: in contrast to the behaviour observed for thiocyanatopalladium(II) complexes, M–NCS bond formation is promoted in solvents having high dielectric constants.

BURMEISTER[1] has recently published a paper with the above title in which he reported that the bonding mode of the co-ordinated thiocyanate ion is dependent upon the nature of the solvent. In particular, he observed that solvents with high dielectric constants promote Pd–SCN bonding when either of the linkage isomers $Pd(AsPh_3)_2(NCS)_2$ or $Pd(AsPh_3)_2(SCN)_2$ are dissolved, whereas solvents with low dielectric constants give rise to a mixture of Pd–NCS, Pd–SCN, and Pd–SCN–Pd bonds. These results prompt us to report some of our results for thiocyanate complexes of a class "a" metal in which the opposite effect is observed.

We have studied the system *trans*-Co(dmg)$_2$L(CNS) (where dmg = dimethylglyoximato- and CNS implies that the mode of bonding of the thiocyanate group is unspecified). We have reported[2] previously the isolation of linkage isomers when L = py. Since the isomers have ν_{CN} bonds at very similar wavelengths (*N*-bonded, 2128 cm^{-1} is higher than *S*-bonded, 2118 cm^{-1} unlike most examples) we have relied on the integrated intensities[3] to characterise the two species, and have supported this evidence with ^1H n.m.r. results: the methyl protons of the dimethylglyoximato-moiety show chemical shifts which are dependent on the nature of the *trans*-ligands.[4]

When Co(dmg)$_2$(py)(SCN) is dissolved in $CHCl_3$, CH_2Cl_2, $CH_2Cl{\cdot}CH_2Cl$, MeCN, or $MeNO_2$ the spectra obtained are similar to that in a KBr disc and show an integrated intensity typical of an *S*-bonded thiocyanate. The spectra do not change significantly with time. The integrated intensities of the same compound in formamide and dimethylformamide show an increasing proportion of the *N*-bonded isomer (although only one peak is observed) suggesting that the principal reaction taking place may be represented by the following equilibrium: $Co(dmg)_2L(SCN) \rightleftharpoons Co(dmg)_2L(NCS)$. The results in $HCONMe_2$ indicated that approximately equal amounts of the two isomers are present after three days: A increases from $1{\cdot}92 \times 10^{-4}$ to $6{\cdot}30 \times 10^{-4}$ M^{-1} cm^2.

The linkage isomer Co(dmg)$_2$(py)(NCS) is generally less soluble, so that fewer solvents are available for its study. In MeCN, $MeNO_2$, and $HCONMe_2$ more than one peak is observed in solution corresponding to the formation of the free ion, and in some cases of the bridging group Co-NCS–Co. There were indications of NCS$^-$ formation in some solvents in the case of Co(dmg)$_2$(py)(SCN), but only in relatively small amounts.

When pyridine is replaced by other ligands *trans* to the thiocyanate group, only one n.m.r. peak is observed for L = 3-chloro-, 3-bromo-, 3-methyl-, and 4-methyl-pyridine in $CDCl_3$ whereas two are present in $(CD_3)_2SO$ for the same complexes. The integrated intensities for these complexes follow a similar pattern, namely they are close to 3×10^{-4} M^{-1} cm^2 in $CHCl_3$ but in the range 5—7 $\times 10^{-4}$ M^{-1} cm^2 in $HCONMe_2$. This effect of solvent operates only in the presence of certain ligands *trans* to the thiocyanate group and not of others: a predominantly *N*-bonded complex is observed in both $CHCl_3$ and $HCONMe_2$ when L = NO_2^-, but *S*-bonding is maintained in both these solvents when L = NH_3.

In general, class "a" metals form *N*-bonded thiocyanate complexes while class "b" metals bond to thiocyanate through sulphur, and the effect of π-bonding ligands is to reverse each of these situations. Thus, $Pd(NH_3)_2(SCN)_2$ and $[Co(NH_3)_5NCS]^{2+}$ are typical examples of mixed-ligand complexes with neutral ligands having no ability to delocalise electrons from the metal whereas, with π-bonding ligands, compounds such as $Pd(PEt_3)_2(NCS)_2$ and [Co(dmg)$_2$ (SCN)$_2$]$^-$ are formed (see ref. 5 for further examples and for references). When our results on solvent effects are compared and contrasted with those of Burmeister,[1] it appears that here is another example of effects acting in different directions on thiocyanate complexes of class "a" and class "b" metals, respectively. Solvents of high dielectric constant favour *S*-bonding in linkage isomers of Pd^{II} (class "b"),[1] but *N*-bonding in linkage isomers of Co^{III} (class "a").

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[1] J. L. Burmeister, R. L. Hassel, and R. J. Phelan, *Chem. Comm.*, 1970, 679.

[2] A. H. Norbury and A. I. P. Sinha, *Inorg. Nuclear Chem. Letters*, 1968, **4**, 617.

[3] C. Pecile, *Inorg. Chem.*, 1966, **5**, 210; R. Larssen and A. Miezis, *Acta Chem. Scand.*, 1969, **23**, 37.

[4] H. A. O. Hill and K. G. Morallee, *J. Chem. Soc.* (*A*), 1969, 554.

[5] A. H. Norbury and A. I. P. Sinha, *Quart. Rev.*, 1970, **24**, 69.