Linkage Isomerism of the Co-ordinated Thiocyanate Ion in Cobalt(III) Complexes

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Summary The *N*-bonded and *S*-bonded isomers of thiocyanatobis(dimethyl glyoximato)(t-butylpyridine)cobalt(III) have been found to undergo cobalt(II) catalysed equilibration in dimethylformamide and dimethyl sulphoxide solution to approximately equal amounts; these results closely parallel one and differ from another study on the analogous pyridine complexes.

Two recent communications[1,2] have reported solution studies of the linkage isomers of (py)Co$(DH)_2$(thiocyanato) (py = pyridine, DH = monoanion of dimethyl glyoxime; thiocyanato does not imply a particular bonding mode). These reports were in substantial disagreement as to the nature of the two species found in solvents such as *NN*-dimethylformamide (DMF) and dimethyl sulphoxide (DMSO). These were thought to be an equilibrium mixture of the *N*- and *S*-bonded isomers in the first study[1,3] and a mixture of a solvate and the *N*-bonded isomer in the second study.[2] We now report our findings on the nature of the analogous 4-t-butylpyridine complexes in solution, and also evidence that isomerization is not an ionic process as previously sugggested.[2]

We have found[4] in every case examined that complexes of the type $LCo(DH)_2X$ (where L and X are neutral and uninegative monodentate ligands, respectively), prepared analytically pure by the usual methods involving air oxidation, contain traces of cobalt(II) impurities ($< 0{\cdot}1\%$). These impurities promoted unexpected reactions [*e.g.* equation (1)] in non-aqueous solvents. Kinetic studies

$$L^1 + L^2Co(DH)_2X \rightarrow L^1Co(DH)_2X + L^2 \qquad (1)$$

indicated that these reactions were most rapid when X was a good bridging ligand for inner-sphere electron-transfer reactions. Such inner-sphere electron transfer *via* a thiocyanate bridge can lead to equilibration of linkage isomers.[7]

Fractional recrystallization of preparative mixtures[3,5,6] from acetone–hexane gave two isomers having the same relative spectral properties as those reported in one study of the pyridine complexes.[3] These are (*N*-bonded *vs.* *S*-bonded): (i) oxime-Me resonance at τ 7·59 *vs.* τ 7·65 (DMSO); and (ii) intense peak for CN stretch at 2110 cm^{-1} *vs.* *ca.* 10 times less intense peak at 2055 cm^{-1} (KBr pellets). The ^{1}H n.m.r. spectra in DMF (relative intensities in parentheses) have peaks at τ 7·58 (1·0) and 8·78 (0·75) (*N*-bonded) and at τ 7·62 (1·0) and 8·75 (0·75) (*S*-bonded), with the upfield peaks assigned to the butyl groups. Peaks attributable to small amounts of the *N*-bonded isomer are found in the spectrum of the *S*-bonded material.

The n.m.r. spectrum of these compounds in DMF or DMSO was unaffected by KSCN and did not change during several weeks if a small amount of oxidizing agent such as $BrCCl_3$ was present or if the isomers had been recrystallized from solutions containing $BrCCl_3$. Otherwise, the *N*- and *S*-bonded materials, after being set aside for several hours in DMF or DMSO solution, had the same n.m.r. spectrum. The addition of small amounts of $(Bu^tpy)Co(DH)_2$ resulted in immediate equilibration. Analysis of both the methyl and butyl signals in the spectra showed that both isomers were present in approximately equal concentrations in DMF, a result similar to that found in one study of the pyridine complexes.[1] In DMSO, the concentration of the *N*-bonded isomer was twice that of the *S*-bonded compound.

The equilibrium position determined from the butyl resonances was unaffected by added KSCN. Unco-ordinated t-butylpyridine was formed, however, and changes in the methyl resonances similar to those observed for the pyridine complexes[2] occurred.

The ratio of the peaks in DMF was concentration independent. This result is consistent with the *S*-bonded $\rightleftharpoons$*N*-bonded equilibrium but inconsistent with the existence of a solvated complex, a higher percentage of which would exist in dilute solution. The i.r. spectrum of the most dilute solution used in the n.m.r. study contained no bands attributable to unco-ordinated SCN$^-$. If one set of resonances were those of the solvate, a large CN stretching band would have been observed at 2050 cm^{-1}. The frequencies of the CN stretching bands of the isomers dissolved in DMF are similar (2100 and 2115 cm^{-1} for the *S*- and *N*-bonded isomers, respectively); for the equilibrated mixture one band with a shoulder at *ca.* 2100 cm^{-1} was observed at 2115 cm^{-1}. The intensity of this band was consistent with approximately equal concentrations of the linkage isomers. Finally, an equilibrated 0·05M-DMF solution (checked by n.m.r.) was diluted to 10^{-3}M. The conductivity of this solution, measured immediately, was the same as that of the solvent ($\pm$ 0·02 $\mu\Omega^{-1}$ cm^{-1}), indicating the absence of a solvated complex.

Equilibration was much more rapid in DMF or DMSO than in CH_2Cl_2, as observed also for the pyridine complexes.[1,2] This solvent dependence led to the argument[2] that equilibration in the pyridine system was an ionic process. However, the present results indicate that equilibration *via* an ionic pathway is not favourable, even in solvents such as DMF and DMSO.

The similarity of our results to those of Norbury and his co-workers[1,3] strongly supports their conclusions and suggests that equilibration of the pyridine complexes is also cobalt(II) catalysed. The conflicting conclusions reached earlier[1–3] can be attributed to differing amounts of catalysts in the samples studied.

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