

## Solvent Control of the Bonding Mode of Co-ordinated Thiocyanate Ion in Cobalt(III) Complexes

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**Summary** The different bonding modes exhibited by the co-ordinated thiocyanate ion when the complex *trans*-Co(dmg)<sub>2</sub>(py)(SCN) is dissolved in high or low dielectric constant solvents have been shown to be kinetically controlled, rather than thermodynamically controlled, as was previously proposed by other workers.

NORBURY, SHAW, and SINHA have recently reported<sup>1</sup> that the bonding mode of the thiocyanate ion in the complex *trans*-Co(dmg)<sub>2</sub>(py)(SCN) (py = pyridine, dmg = dimethylglyoximate) in solution is solvent dependent, N-bonding being preferred in solvents having high dielectric constants and S-bonding being retained in low dielectric constant solvents. They cited this system as an example of solvent control of the bonding mode of an ambidentate ligand in opposition to that previously reported,<sup>2</sup> wherein Pd-SCN bonding is favoured in high dielectric constant solvents and Pd-NCS bonding is favoured in low dielectric constant solvents. Since our observations were in accord with the predictions afforded by Klopman<sup>3</sup> wherein no distinction is made between class 'a' and class 'b' metal ions, we have investigated the Co(dmg)<sub>2</sub>(py)(SCN) system, and have found that the conclusions reached by Norbury, *et al.*<sup>1</sup> with regard to solvent control of the thiocyanate bonding mode are erroneous.

Both linkage isomers of *trans*-Co(dmg)<sub>2</sub>(py)(SCN) were prepared, the S-bonded isomer by the method of Norbury and Sinha,<sup>4</sup> the N-bonded isomer by the method of Chugaev.<sup>5</sup> They were characterized by their  $\nu(\text{CN})$  frequencies (S-bonded, 2118; N-bonded, 2128 cm<sup>-1</sup>) and integrated absorption intensities in acetone solution and in the solid state (KBr disks, salicylic acid internal standard).<sup>6</sup>

A solution of the S-bonded isomer in dimethylformamide (DMF) exhibits only one  $\nu(\text{CN})$  peak,<sup>1</sup> the integrated absorption intensity of which increases with time, indicating an increasing proportion of the N-bonded isomer (a weak peak characteristic of ionic SCN<sup>-</sup> also appears with time). Isomerization was almost complete after three days. In dimethyl sulphoxide (DMSO) solution, the results were even more dramatic, isomerization to the N-isomer being almost complete during the time required for dissolution of the sample (extensive ionization also occurs). Likewise, as reported earlier,<sup>1</sup> solutions of the S-bonded isomer in CHCl<sub>3</sub>, acetone, and MeCN exhibit  $\nu(\text{CN})$  integrated absorption intensities which are characteristic<sup>7</sup> of S-bonded

thiocyanate and which do not change with time. However, we have found that the N-bonded isomer *also* does not isomerize in CHCl<sub>3</sub>, acetone, or MeCN nor, for that matter, in CH<sub>2</sub>Cl<sub>2</sub>, DMF or DMSO (some ionization occurs in MeCN, DMF, and DMSO). The  $\nu(\text{CN})$  integrated absorption intensities observed are characteristic<sup>7</sup> of N-bonded thiocyanate and do not change appreciably with time.

Thus, unlike the Pd<sup>II</sup>-thiocyanate system,<sup>2</sup> where the equilibrium Pd-SCN: Pd-NCS ratio is markedly solvent-dependent, these results indicate that the different behaviour of Co(dmg)<sub>2</sub>(py)(SCN) in high compared with low dielectric solvents is not due to thermodynamic solvent control but is, instead, a kinetic effect. The S → N-bonded isomerization probably occurs *via* a dissociative or ion-pair mechanism, since, in solvents with high dielectric constants like DMF and DMSO, the rate of isomerization is relatively rapid. These solvents can lower the activation energy for isomerization by providing better solvation of the free ion and, as would be expected, relatively large concentrations of non-co-ordinated SCN<sup>-</sup> are formed in these solutions. In low dielectric constant solvents, no appreciable isomerization was observed after 30 days at room temperature. However, the same S → N-bonded isomerization can be effected in these solvents by raising the temperature (isomerization to the N-bonded isomer is essentially complete after several h reflux in acetone or CHCl<sub>3</sub>). Once formed, the N-bonded isomer is stable indefinitely in solution. Isomerization to the N-bonded isomer also occurs in the solid state over a period of months.

Hill and Morallee have shown<sup>8</sup> that the methyl protons of the dmg<sup>-</sup> moiety exhibit n.m.r. chemical shifts which depend on the axial groups in similar cobalt(III) compounds, the  $\tau$  value for the protons being a function of the Hammett  $\sigma$  strength of the axial ligands. Norbury and Sinha assigned<sup>4</sup> peaks at  $\tau$  7.67 and 7.62 for the S- and N-bonded isomers, respectively, in DMSO solution. Our studies seem to indicate, however, that the n.m.r. technique is not sensitive enough to make such a differentiation, and that these peak assignments are incorrect.

The n.m.r. spectra of solutions of *either* pure isomer in CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, MeCN, or acetone exhibit a single peak in the range  $\tau$  7.62—7.64 which does not change with time. Thus, the  $\tau$  value does not reflect the bonding mode of axial thiocyanate, since isomerization does not take place in these solvents at room temperature. The spectrum of a

DMF solution exhibits methyl resonances at  $\tau$  7.59 and 7.67, while that of a DMSO solution includes peaks at  $\tau$  7.62 and 7.67, the spectra again being independent of the isomer initially introduced and invariant with time. The peak at  $\tau$  7.67 is assigned to the thiocyanate complex, whereas the  $\tau$  7.59 and 7.62 peaks are assigned to complexes containing a solvent molecule in the axial position (the i.r. data indicate that some ionization takes place in these solvents). These assignments are also supported by the observation that addition of solid KSCN to the DMSO solution results in a *reduction* of the 7.62  $\tau$ :7.67  $\tau$  peak height ratio. The slight differences in the  $\tau$  values for the thiocyanate-containing complex are a result of the different co-ordinating properties of the solvents. The coincidence of the peak of the thiocyanate compound in the first group

of solvents with that of the solvated species in DMSO is fortuitous.

As mentioned earlier, solvent control of ambidentate bonding modes should be possible in class 'a' systems such as  $\text{Co}^{\text{III}}$  as well as in class 'b' systems such as  $\text{Pd}^{\text{II}}$ . The tendency<sup>9,10</sup> of  $\text{Co}(\text{CN})_5\text{XCN}^{3-}$  ( $\text{X} = \text{S},^9 \text{Se}^{10}$ ) complexes to isomerize to their N-bonded isomers in  $\text{CH}_2\text{Cl}_2$  solution, while remaining largely X-bonded in aqueous solution provides experimental verification of this prediction. In the case of  $\text{Co}(\text{dmg})_2(\text{py})(\text{SCN})$ , the N-bonded isomer is so thermodynamically favoured that solvent control is obliterated.

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<sup>1</sup> A. H. Norbury, P. E. Shaw, and A. I. P. Sinha, *Chem. Comm.*, 1970, 1080.

<sup>2</sup> J. L. Burmeister, R. L. Hassel, and R. J. Phelan, *Chem. Comm.*, 1970, 679.

<sup>3</sup> G. Klopman, *J. Amer. Chem. Soc.*, 1968, **90**, 223.

<sup>4</sup> A. H. Norbury and A. I. P. Sinha, *Inorg. Nuclear Chem. Letters*, 1968, **4**, 617.

<sup>5</sup> L. A. Chugaev, *Ber.*, 1907, **40**, 3498.

<sup>6</sup> R. A. Bailey, S. L. Kozak, T. W. Michelsen, and W. N. Mills, *Co-ordination Chem. Rev.*, in the press.

<sup>7</sup> C. Pecile, *Inorg. Chem.*, 1966, **5**, 210.

<sup>8</sup> H. A. O. Hill and K. G. Morallee, *J. Chem. Soc. (A)*, 1969, 554.

<sup>9</sup> D. F. Gutterman and H. B. Gray, *J. Amer. Chem. Soc.*, 1969, **91**, 3105.

<sup>10</sup> J. L. Burmeister and J. B. Melpolder, unpublished results.