Antisymbiosis and the *trans*-Effect in Gold(I) Thiocyanate Complexes

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Summary An antisymbiotic bonding trend has been observed for a series of solutions of linear LAu(thiocyanate) complexes, *i.e.*, in a constant steric environment, irrespective of the solvent used, the Au–NCS/Au–SCN ratio increases as the *trans*-effect of the L ligand increases.

Following the introduction of Pearson's hard–soft acid–base principle,[1] two notable, related categories of behaviour have been observed: symbiosis in class (a) complexes[2] and anti-symbiotic *trans*-effect or influence in class (b) complexes.[3] Ambidentate ligands such as (SCN^-) and ($SeCN^-$) ions would appear to be ideal probes of both theories, since both ions possess both hard and soft donor atoms. Unfortunately, the unambiguous interpretation of ligand effects on the bonding mode of the thiocyanate ion in class (b) complexes, *e.g.*, those of Pd^{II} and Pt^{II}, has generally been thwarted by the existence of concurrent electronic and steric effects.

Accordingly, we have sought to synthesise a series of thiocyanate-containing complexes of a class (b) metal containing other ligands of varying *trans*-directing ability wherein the steric environment was maintained essentially constant. The linear gold(I) complexes of the type LAu(thiocyanate) appeared to be ideal for this study; however, no infrared evidence had been observed[4] for the existence of anything other than LAu–SCN species, either in the solid state or in dichloromethane solution. By using an i.r.solution cell having a greater path length (1 mm instead of 0·1 mm), it became apparent that the LAu–NCS isomer was indeed present in some of the solutions and, significantly, the amount of the N-bonded isomer present varied as a function of L.

Table. Au–NCS/Au–SCN *ratios for a series of* LAu *(thiocyanate) complexes in solution.*

Complex	Au–NCS/Au–SCN Ratio[a]	Other solvents used
$Au[P(OPh)_3]SCN$	1·57	b,c,d
$Au(PMe_3)SCN$	0·67	c,d,e,f,g
$Au(PPh_3)SCN$	0·52	b,c,d,e,f,g
$Au(AsPh_3)SCN$	>0	b,c,d,e,f,g
$Au[S(CH_2Ph)_2]SCN$	0	c
Au(etu)SCN[h]	0	f
$Au(PPh_3)SeCN$	0	b,c,d,e,f,g

[a] Ratio measured in $ClCH_2CH_2Cl$ (see text). [b] Benzene. [c] Nitrobenzene [d] Acetonitrile. [e] Dichloromethane. [f] Acetone. [g] Me_2SO. [h] etu = ethylenethiourea.

Shown in the Table are the Au–NCS/Au–SCN ratios, measured as the ratio of the areas under the curves of the N- and S-bonded ν_{CN} bands at, respectively, *ca.* 2080 cm^{-1} and *ca.* 2125 cm^{-1} for several representative LAu(thiocyanate) complexes dissolved in 1,2-dichloroethane. The complexes are listed in decreasing order of the *trans*-directing ability of the L ligand. Also shown are the other solvents in which measurements were made. None of the solutions exhibited a ν_{CN} band at *ca.* 2050 cm^{-1} which would be due[5] to the formation of ionic SCN$^-$.

The N-bonded isomer is a minor or non-existent component in all of the solutions, since the integrated absorption intensity of the ν_{CN} band of an N-bonded thiocyanate is generally about an order of magnitude larger than that of an S-bonded thiocyanate.[5] Nonetheless, it is clear that the proportion of the N-bonded isomer present increases as the *trans*-influence of the L ligand increases, completely in accord with Pearson's antisymbiotic *trans*-influence principle.[3] It should also be noted that the Au(PPh$_3$)SeCN complex gave no evidence of isomerization, in accord with the greater soft character of the selenium atom.

Since the bonding mode adopted by the thiocyanate ion in solution has been shown to be influenced by the nature of the solvent for both class (b)[6] and class (a)[7] complexes, the Au–NCS/Au–SCN ratio was also measured for most of the complexes in a variety of solvents of varying dielectric constant. Although the absolute value of the ratios changed slightly from solvent to solvent, the order did not, lending further credence to the basic conclusion.

We thank the National Science Foundation for financial support and Prof. Pearson for stimulating discussions and a copy of his paper prior to publication.

(*Received*, 1*st June* 1973; *Com.* 786.)

[1] R. G. Pearson, *J. Amer. Chem. Soc.*, 1963, **85**, 3533.

[2] C. K. Jørgensen, *Inorg. Chem.*, 1964, **3**, 1201.

[3] R. G. Pearson, *Inorg. Chem.*, 1973, **12**, 712.

[4] N. J. DeStefano and J. L. Burmeister, *Inorg. Chem.*, 1971, **10**, 998; also see *Chem. Comm.*, 1970, 1698.

[5] J. L. Burmeister, *Co-ordination Chem. Rev.*, 1968, **3**, 225.

[6] J. L. Burmeister, R. L. Hassel, and R. J. Phelan, *Inorg. Chem.*, 1971, **10**, 2032; also see *Chem. Comm.*, 1970, 679.

[7] L. G. Marzilli, *Inorg. Chem.*, 1972, **11**, 2504; also see *J.C.S. Chem. Comm.*, 1972, 109.