

Mitchell P C H & Williams R J P. The infrared spectra and general properties of inorganic thiocyanates. *J. Chem. Soc.* 1960:1912-18.
[Inorganic Chemistry Laboratory, Oxford University, England]

For thiocyanato complexes, C-N vibration frequencies were correlated with the thiocyanate binding, M-NCS, M-SCN, or M-NCS-M. The binding preference, -NCS or -SCN, of a cation was related to the relative importance of electrostatic and covalent contributions to the bonding. Our conclusions were generalised to other ligands. We discussed critically π -bonding and ligand-field strengths. [The SCI® indicates that this paper has been cited in over 285 publications since 1961.]

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"The paper was written while I was a graduate student with R.J.P. Williams at Oxford University. It was a spin-off from my research topic, molybdenum coordination chemistry. Our interest was in the biological role of molybdenum, but first we had to sort out the coordination chemistry. I read up on molybdenum in Sidgwick's *The Chemical Elements and Their Compounds*, still a classic.¹ A compound which looked interesting was the red-brown molybdenum(V) thiocyanate complex, (pyridinium) [MoO₂(NCS)₃]. The formula suggested five-coordinate molybdenum, possibly an unsaturated molybdenum atom of the type we might imagine to bind substrate molecules in a molybdoenzyme. We made the compound, but it turned out to be diamagnetic, a dimer with six-coordinate molybdenum(V).

"The work developed in two directions: the chemistry of oxomolybdenum species² and the structure and bonding of thiocyanates. To write a structure we needed to know whether NCS was bound to molybdenum through nitrogen or sulphur. To solve this problem, before X-ray crystallography was routine, we used infrared spectroscopy. The position of the C-N stretching vibration had already been used to decide between

bridging and terminal thiocyanate. I made a large number of thiocyanate complexes and recorded their ir spectra in the Dyson Perrins Laboratory (organic chemistry) because the Inorganic Chemistry Laboratory did not possess an ir spectrometer. It was not then a technique much used by inorganic chemists. The C-N vibration frequency decreased from bridging to S-bound to N-bound thiocyanate but the correlations were blurred by other structural factors. There was, however, no doubt that the molybdenum-thiocyanate binding was through nitrogen (later confirmed by X-ray crystallography), so we had solved the problem we started with. We went on to discuss the reasons for the observed orientation of thiocyanate to different cations. Thiocyanate, in presenting cations with a choice of N- or S-binding, is a good test of binding preferences. The paper stressed the relative importance of electrostatic and covalent binding, rather than π -bonding and the spectroscopically derived, alleged ligand-field strengths, then very much in vogue.

"My contribution was to make the compounds, measure and sort out the spectra, and then with Williams, my supervisor, to discuss the wider implications. Doing the work taught me a lot about getting and sorting out data and, while not overdoing the interpretation, looking at the wood as well as the trees. I continued in molybdenum chemistry, mostly with sulphur ligands. Our paper showed a clear class a behaviour on the part of molybdenum. It is perhaps ironic that the biological chemistry of molybdenum, which was our starting point, is dominated by molybdenum-sulphur interactions.

"Why has our paper been frequently cited? We set up ir spectroscopic criteria, still useful, for thiocyanate binding and we established thiocyanate as a probe for cation binding preferences. Our paper has been followed by work on thiocyanate and other ambidentate ligands using many different structural and spectroscopic techniques.³ Also, we generalised to other ligands. Our paper was central to the discussion, still continuing,⁴ and highlighted in biological inorganic chemistry,⁵ of the facts and theories of cation-ligand binding."

1. Sidgwick N V. *The chemical elements and their compounds*.

Oxford: Clarendon Press, 1950. Vol. II. p. 1028-68.

2. Mitchell P C H. Oxo-species of molybdenum-(V) and -(VI). *Quart. Rev.* 20:103-18, 1966.

3. Barmeister J L. Coordination chemistry. (Newman A A, ed.) *Chemistry and biochemistry of thiocyanic acid and its derivatives*. London: Academic Press, 1975. p. 68-130.

4. Williams R J P & Hale J D. Classification of acceptors and donors in inorganic reactions. *Struct. Bond.* 1:249-81, 1966.

5. Frusto da Silva J J R & Williams R J P. The uptake of elements by biological systems. *Struct. Bond.* 29:69-121, 1976.